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RUBBER CHEMISTRY AND TECHNOLOGY

PUBLISHED IN FIVE ISSUES BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY

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BLACKS

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UNITED CARBON BLACKS have been recognized for their dependability and general excellence for more than three decades.

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A — **Philblack A, Fast Extrusion Furnace Black.** Excellent tubing, molding, calendering, finish! Mixes easily. Disperses heat. Non-staining.

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Polysar Latex II — Polysar Latex IV — Polysar Latex 721

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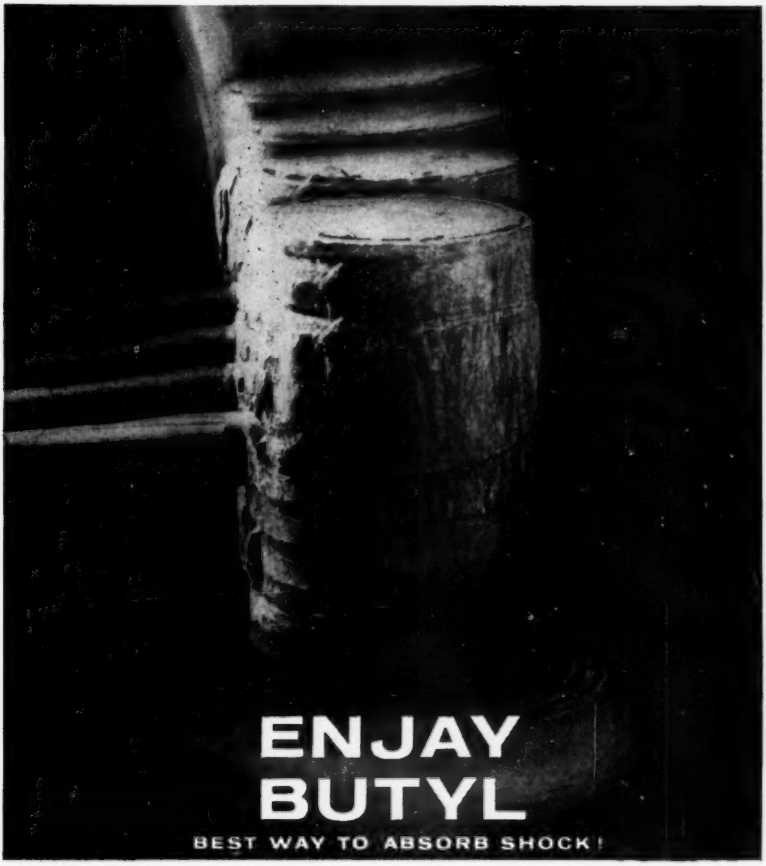

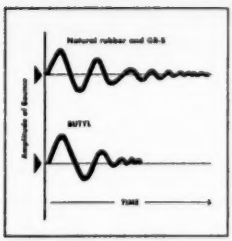

Butyl's superior shock-absorption characteristics reduce amplitude of bounce in much less time as compared with other rubbers.

Enjay Butyl, because of its higher damping factor, absorbs shock energy *more* completely than any other rubber. Through simple variations in compounding or processing, you can build the right degree of resiliency for your requirements. Butyl is the ideal rubber for motor mounts, load cushions, sound deadener insulation, axle and body bumpers—and other shock, noise and mechanical-vibration applications.

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Find out how this versatile rubber can improve your product. Call or write the Enjay Company, today!

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DEPENDABLE IN PERFORMANCE . . . UNIFORM IN QUALITY

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Accelerator 833
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MBT
MBTS
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Tepidone
Tetrone A
Thionex
Thionex Grains
Thiuram E
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Hylene* M-50
Hylene* MP
Hylene* T
Hylene* TM
Hylene* TM-65

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RPA No. 3 Concentrated
RPA No. 6
RR-10

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BARAK—Retarder activator for thiazole accelerators

Copper Inhibitor 65—Inhibits catalytic action of copper on elastomers

ELA, ELA-N—Elastomer lubricating agents

HELIOZONE—Sun-checking inhibitor

NBC—Inhibits weather and ozone cracking of SBR compounds. Improves heat and sunlight discoloration resistance of neoprene stocks.

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Retarder-activator for acidic accelerators. Also an activator for certain blowing agents.

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Elastomer Chemicals Department

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Better Things for Better Living
. . . through Chemistry

MILL SHRINKAGE TEST

(Stock placed on cold mill, preset at .050" between rolls. After stock warmed, samples cut and permitted to cool)

HARDNESS:					
80 DUROMETER					
40 DUROMETER					
STOCK COMPOSITION:	0% CHEMIGUM N-8 100% Polymer "A"	25% CHEMIGUM N-8 75% Polymer "A"	50% CHEMIGUM N-8 50% Polymer "A"	75% CHEMIGUM N-8 25% Polymer "A"	100% CHEMIGUM N-8 0% Polymer "A"

How to improve the run of your mill

The samples above tell the story. Taken from a series of test mill runs, they graphically illustrate the superior processability of new CHEMIGUM N-8 and how it can be used to improve the processing of other nitrile rubbers.

CHEMIGUM N-8 is an intermediate acrylonitrile content copolymer and exhibits corresponding oil resistance and physical properties. It also exhibits very rapid mill breakdown and will form a smooth sheet immediately, even on a cold mill.

By blending CHEMIGUM N-8 with other nitrile, styrene or natural rubbers, processing characteristics and physical properties can be obtained which previously were not possible. And, since it is stabilized with a nonstaining, non-discoloring antioxidant, it can be used in the most exacting color applications. For full details on unusual CHEMIGUM N-8, including the latest *Tech Book Bulletins*, just write to Goodyear, Chemical Division, Dept. V-9430, Akron 16, Ohio.

GOODYEAR

CHEMICAL DIVISION

Chemigum—T.M. The Goodyear Tire & Rubber Company, Akron, Ohio

Rubber samples (ASTM bent loops) after 72 hr. exposure to 40 pphm ozone at 100° F. Severely damaged sample is a high-cost polymer cured 40 min. at 298° F. and supposedly stable against ozone attack. The other is an SBR formulation containing 3 phr UOP 88, cured 40 min. at 284° F.

NOW...prevent ozone damage, cut product cost, too!

SBR compound with UOP antiozonant withstands ozone better than supposedly stable high-cost polymer— yet costs substantially less!

The rubber test strips shown above tell a story that's mighty important to your profit picture. In addition to the obvious superiority of one over the other is this significant fact:

The test strip riddled with cracks is a high-cost polymer used for its resistance to ozone—the other a conventional SBR polymer protected with UOP antiozonant at substantially lower overall cost.

When you include UOP 88 or 288 in your formulation, the versatile chemical barrier slowly and uniformly migrates to vulnerable rubber surfaces—and thus keeps your product free of unsightly, degrading cracks throughout its entire life, regardless of the severity of conditions to which it may be subjected.

Using UOP 88 and 288 antiozonants you produce a top quality ozone-resistant product at minimum cost. Can you afford to do otherwise? Detailed information and samples are yours for the asking. Just write our Products Department.

UOP

UNIVERSAL OIL PRODUCTS COMPANY

30 Algonquin Road, Des Plaines, Illinois, U.S.A.

More Than Forty Years Of Leadership In Petroleum Refining Technology

QUALITY PRODUCTS for the RUBBER INDUSTRY

General Tire's Chemical Division is constantly aware of the needs of the rubber industry, and provides these specially-formulated products to meet those needs. Write or call for further information and generous samples.

RUBBER CHEMICALS:

GEN-TAC • Vinyl pyridine latex. Assures excellent fabric-to-rubber adhesion using nylon or rayon cords.

KO-BLEND • Latex-compounded masterbatch, 85% insoluble sulfur colloidally dispersed in GRS latex. Cuts whitewall rejects and reworks . . . eliminates spots, streaks and batch softening.

KURE-BLEND MT • 50 GRS—50 TMTD latex-compounded masterbatch. Gives faster, more even dispersion, allowing full advantage of TMTD accelerator. Assures uniform cure, at no premium cost.

RUBBER:

GENTRO • Top-quality cold SBR Polymers.

GENTRO-JET • Cold and oil-extended black masterbatches, for easier processing and more efficient production.

LATICES:

GEN-FLO • Styrene-butadiene, with balanced stabilization system, low odor, and excellent mechanical stability.

ACRI-FLO • Styrene-acrylic, offering excellent adhesion, mechanical stability and UV heat and light stability.

PVC RESINS:

VYGEN • a complete family of top-quality, versatile resins formulated to meet specific needs.

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Creating Progress Through Chemistry

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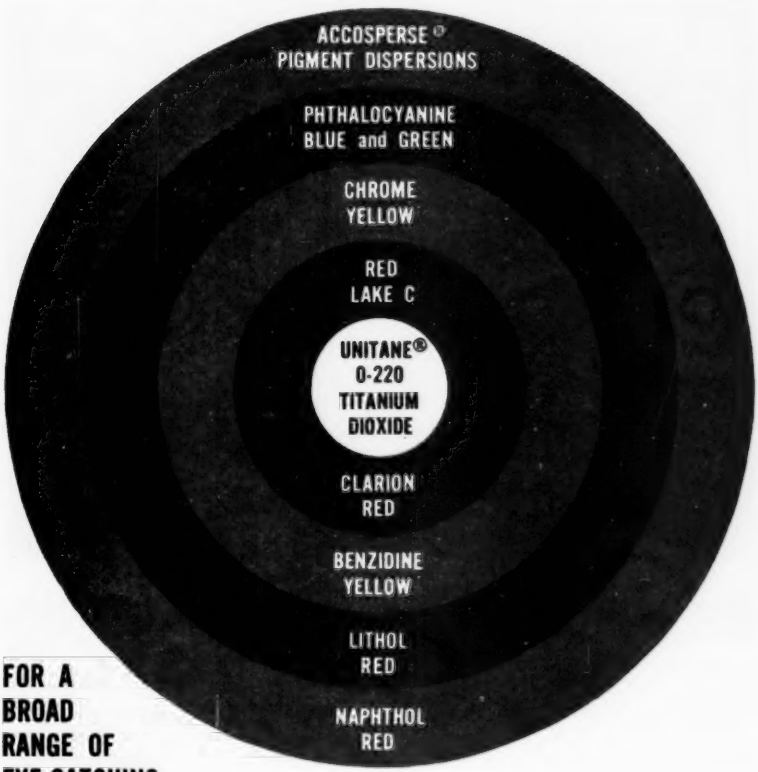
THE GENERAL TIRE & RUBBER CO.



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CYANAMID PIGMENTS

Whatever your aim in hue, you'll find it in Cyanamid's line of pigments. You will also benefit from their excellent formulating properties.

Call your Cyanamid Pigments representative for technical information and samples.

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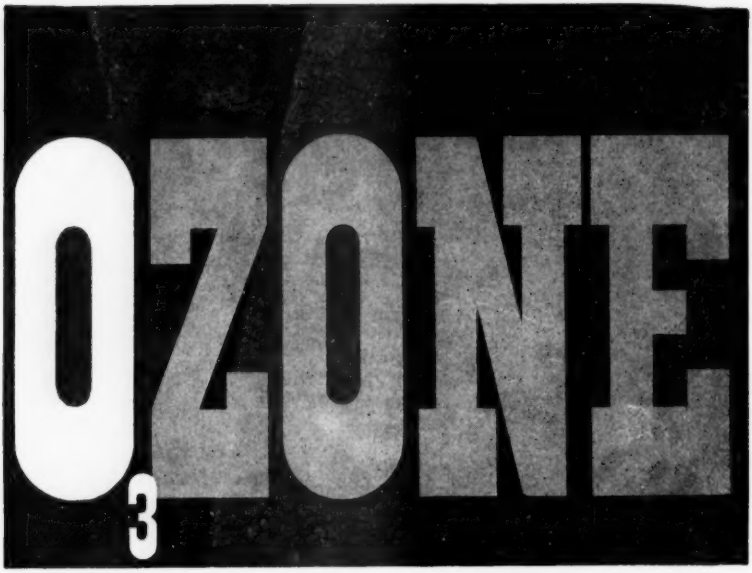

How to arrest its attack on rubber products

Ozone attack is now recognized as the major cause of cracking and checking in stressed rubber products.

The mechanism of this deterioration is attributed to the chemical attack of ozone upon the carbon-to-carbon double bonds of unsaturated elastomers. Through a complex reaction the double bond is broken. This places additional stress upon adjacent chains, increasing their sensitivity to attack. Thus a continuing reaction occurs, leading to development of fissures perpendicular to the direction of stress.

To combat the deteriorating effects of ozone attack, rubber chemists are turning to antiozonants. Easily incorporated into the rubber during processing, antiozonants slowly exude to the surface during use to provide continuing protection.

Eastozone antiozonants protect rubber products more effectively at lower cost than do other types of commercially-used antiozonants. Compounders often can cut antiozonant requirements in half and still get the same ozone resistance, using Eastozone antiozonants.

For samples of Eastozone and further information, contact the Eastman representative nearest you or write to EASTMAN CHEMICAL PRODUCTS, INC., subsidiary of Eastman Kodak Company, KINGSPORT, TENNESSEE.

Eastozone **Eastman Rubber Antiozonants**

SALES OFFICES: Eastman Chemical Products, Inc., Kingsport, Tennessee; Atlanta; Chicago; Cincinnati; Cleveland; Detroit; Framingham, Massachusetts; Greensboro, N. C.; Houston; New York City; St. Louis.
West Coast: Wilson Meyer Co., San Francisco; Los Angeles; Portland; Salt Lake City; Seattle.

NOW THERE ARE THREE COLUMBIA-SOUTHERN CALCENE® PIGMENTS

Calcene CO, a new grade of calcium carbonate, is the latest of Columbia-Southern's outstanding Calcene white reinforcing pigments. So now you have a choice of *three:*

CALCENE® TM	CALCENE® NC	CALCENE® CO
(Original product) Surface-coated for fast and thorough dispersion.	(Non-Coated) Better in color than TM, but slightly harder dispersing.	(Coated) Clean white to provide true color values in finished goods.

Calcene may provide your rubber products with additional advantages required for better looks, better wear, better price. Use Calcene for pastel or colored goods . . . for improved hot tear resistance . . . for an equivalent high level of uniform physicals at greater economy compared with more costly ultra-fine carbonates. Local stocks provide fast service in Boston, Hoboken, Chicago and Los Angeles. Why not investigate Calcene right now? Price information and formulation suggestions may be obtained by contacting your nearest Columbia-Southern office or by writing Room 1929, One Gateway Center, Pittsburgh 22, Pennsylvania.

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A Subsidiary of Pittsburgh Plate Glass Company • One Gateway Center, Pittsburgh 22, Pa.
DISTRICT OFFICES: Cincinnati • Charlotte • Chicago • Cleveland • Boston • New York • St. Louis
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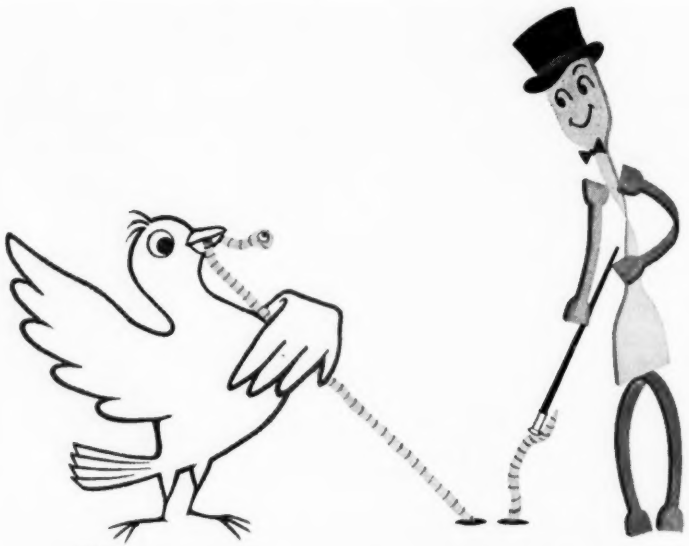

You get easy extrusions with **Philprene***!

CURRENT PHILPRENE POLYMERS		
	NON-PIGMENTED	PIGMENTED WITH PHILBLACK*
HOT	PHILPRENE 1000 PHILPRENE 1001 PHILPRENE 1006 PHILPRENE 1009 PHILPRENE 1010 PHILPRENE 1018 PHILPRENE 1019	
COLD	PHILPRENE 1500 PHILPRENE 1502 PHILPRENE 1503	PHILPRENE 1603** PHILPRENE 1605 **Pigmented with EPC Black
COLD OIL	PHILPRENE 1703 PHILPRENE 1708 PHILPRENE 1712	PHILPRENE 1803 PHILPRENE 6605 PHILPRENE 1805 PHILPRENE 6608 PHILPRENE 6604 PHILPRENE 6620

Operational difficulties are for the birds! The correct Philprene rubber will give you easy extrusions, plus superior physical properties as well! There are many Philprene polymers to choose from, each with its own specific advantages.

Check with your Phillips technical representative. His knowledge and Phillips long experience with rubber, plus the facilities of an up-to-date technical service laboratory, are at your service. This valuable technical assistance can mean a definite increase in your profits.

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QUESTION: *What delayed-action sulfenamide accelerators are my easiest-to-use, surest protection against scorch?*

ANSWER: *New Santocure and Santocure NS "Briquettes"*

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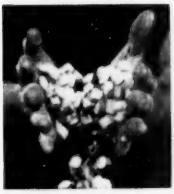
WON'T BRIDGE!

ALWAYS FLOW FREELY, BUT WON'T ROLL

Look how new BRIQUETTES of Santocure and Santocure NS give you more plant-handling ease and convenience. Free-flowing BRIQUETTES won't pack, "bridge," and surge like dry powders—are ideal for automatic weighing or scoop handling. No weighing losses. No rolling! No sticking to the throat or ram of the banbury. Now, with maximum ease of weighing and handling, you can be sure of the delayed-action, safer cures that the Santocures are known to give.

Still the most popular and lowest cost, Santocure was the first uniformly successful sulfenamide accelerator. Powerful Santocure NS gives even greater safety from scorch—up to 10% less accelerator may be used for similar fast, flat curing rates.

Whenever scorch problems threaten...from more rapid processing, higher temperatures, thicker sections, greater activation from reinforcing furnace blacks...try Santocure or Santocure NS BRIQUETTES. Write for sample and technical help in your application.

LET MONSANTO RUBBER CHEMICALS ANSWER YOUR NEXT COMPOUNDING QUESTION

Jot it down on the nearest sheet of paper and send it in with your return address. No obligation—no salesman will call (unless you so request). To help you solve specific problems, Monsanto draws from basic knowledge of more than 85 rubber chemicals and over 18,000 compounding studies. Write, today.

SANTOCURE: MONSANTO T. M., REG. U. S. PAT. OFF.

For sample, use handy coupon

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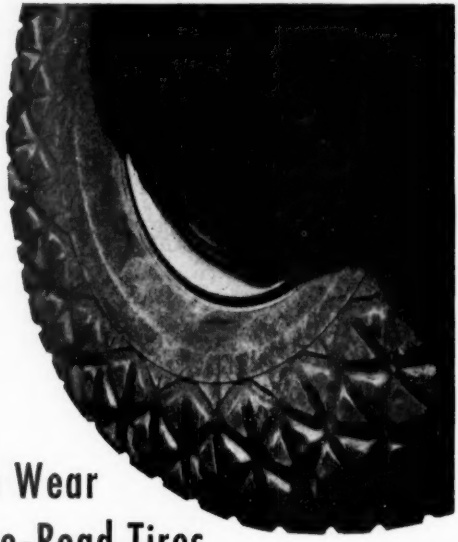

for Down-to-Earth Wear in Off-the-Road Tires

CABOT VULCAN®6* and VULCAN®9**

OFF-THE-ROAD TIRES require the cut-and-chip resistance of Cabot's Vulcan 6 ISAF* or Vulcan 9 SAF** carbon blacks. For heavy duty tires that can withstand the roughest kind of off-the-road wear and tear, use Vulcan 6 or Vulcan 9 in your rubber compounds. Both blacks are recommended for the manufacture of tires used in mining, logging, oil field, construction, and all other off-the-road operations where the going is "rough and tough."

CHANNEL BLACKS:	Spheron 9 EPC	Spheron 6 MPC	Spheron C CC	
FURNACE BLACKS:	Vulcan 9 SAF	Vulcan 6 ISAF	Vulcan 3 HAF	Vulcan XC-72 ECF
	Vulcan SC SCF	Vulcan C CF	Sterling 99 FF	Sterling SO FEF	Sterling V GPF
	Sterling L HMF	Sterling LL HMF	Sterling S SRF	Sterling NS SRF	Pelletex SRF
	Pelletex NS SRF	Sterling R SRF	Gastex SRF		
THERMAL BLACKS:	Sterling FT	Sterling MT	Sterling MT-NS		

Vulcan 6 Intermediate Super Abrasion Furnace Black
**Vulcan 9 Super Abrasion Furnace Black*

Free Samples, Technical Literature Available

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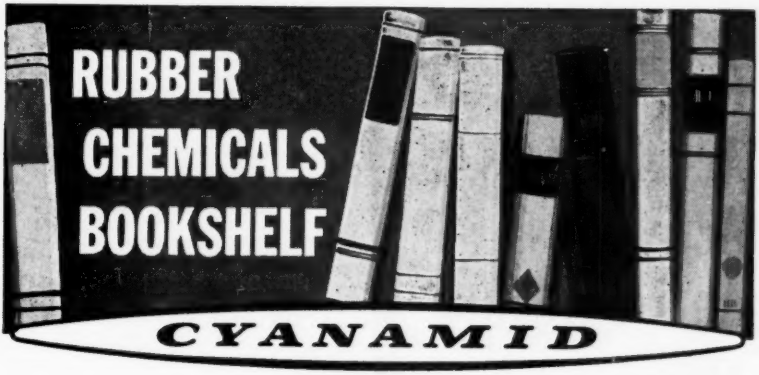

The need of compounders and development chemists for dependable information on commercial rubber chemicals is appreciated by the Rubber Chemicals Department at Cyanamid. The literature listed below has been prepared to meet the critical requirements of rubber manufacturers.

ANTIOXIDANT 2246®
The use of this powerful and non-discoloring antioxidant in various formulas is described. (*Bull. No. 815-B*)

ANTIOXIDANT 425®
Contains information on the use of this premium grade antioxidant in white rubber stocks where minimum discoloration is paramount. (*Bull. No. 840*)

THIAZOLE ACCELERATORS—MBT and MBTS
Formulating data as well as compounding characteristics are shown.
(*Bull. No. 839*)

CYDAC* ACCELERATOR FLAKED
Describes and gives data on this well-known accelerator (N-cyclohexyl benzothiazole-2-sulfenamide) now available in flaked form.

DELAYED-ACTION ACCELERATORS NOBS® No. 1; NOBS® Special
Contains compounding information and performance graphs on these two delayed-action accelerators.
(*Bull. No. 836*)

DIBS® DELAYED-ACTION ACCELERATOR
Describes this new extra-delayed-action accelerator that is especially suitable for higher and more critical processing temperatures. (*Bull. No. 850*)

GUANIDINES DPG and DOTG
Describes these products as primary accelerators and as activators with thiazoles. (*Bull. No. 848*)

2-MT ACCELERATOR
Gives data on this fast-curing accelerator for certain natural GR-S stocks and for latex.

RETARDER PD—AN ANTI-SCORCH AGENT
Discusses the use of this anti-scorch agent with thiazole or activated thiazole-type accelerators. (*Bull. No. 851*)

PEPTON® 22 Plasticizer
The application of this catalytic peptizer in natural and synthetic rubbers is reported. (*Bull. No. 816*)

PEPTON® 22 Plasticizer in Oil-Extended GR-S
Gives test results under conditions approximating those in the factory.
(*Bull. No. 816 Sup. No. 1*)

PEPTON® 65 and 65B Plasticizers
Describes these concentrated peptizers and their application to reduce milling time.

The above literature is available on request.

*Trademark

CYANAMID

AMERICAN CYANAMID COMPANY
RUBBER CHEMICALS DEPARTMENT
Bound Brook, New Jersey

For Accelerators, Activators, Anti-Oxidants and Special Rubber Chemicals

TRY NAUGATUCK

NAUGATUCK supplies a complete line of proven accelerators, activators, anti-oxidants, and special chemicals to give you thorough control of rubber product manufacture and performance.

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THIAZOLES—
M-B-T
M-B-T-S O-X-A-F

THIURAMS—
MONEX*† TUEX†
MORFEX ETHYL TUEX†
PENTEX*

DITHIOCARBAMATES—
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BUTAZATE* METHAZATE*†
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BEUTENE* HEPTEEN BASE*
TRIMENE* TRIMENE BASE*

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SPECIAL PRODUCTS FOR SYNTHETIC POLYMERS

DDM—modifier
THIOSTOP K&N—short stops
POLYGARD—stabilizer

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Plastics
Reclaimed Rubber
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Latices

Write, on your letterhead, for technical data or assistance with any Naugatuck product.

†these products furnished either in powder form or fast-dispersing, free-flowing NAUGETS.

Naugatuck Chemical

Division of United States Rubber Company
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US RUBBER

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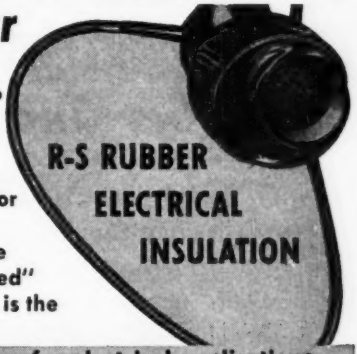

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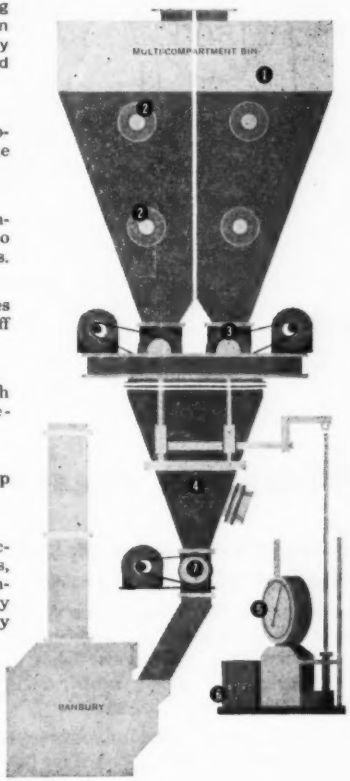

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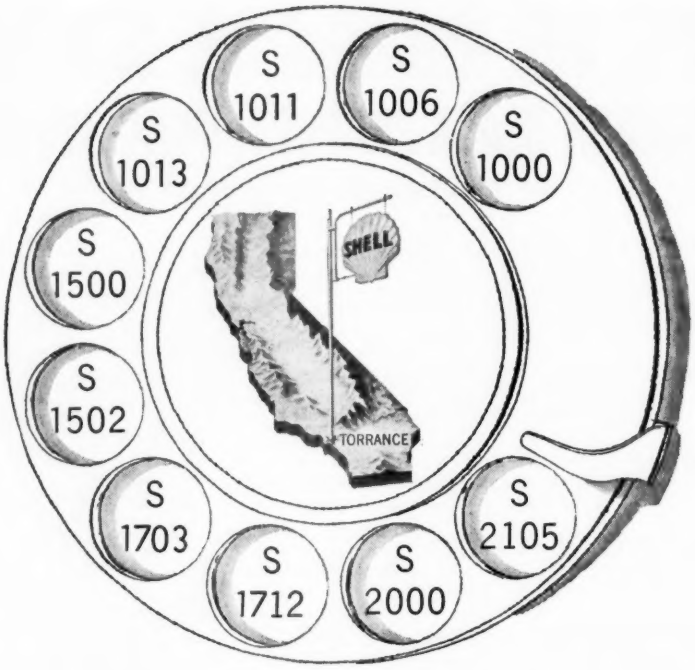

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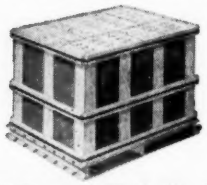

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1960	Spring	Buffalo	Statler	May 3–6
1960	Fall	New York	Commodore	Aug 28–Sept 3
1961	Spring	Louisville	Brown	April 18–21
1961	Fall	Chicago	Sherman	September 5–8
1962	Spring	Boston	Statler	May 15–18
1962	Fall	Atlantic City, N. J.	Chalfonte	September 11–14

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Chairman: W. F. Miller (Yale Rubber & Mfg. Co., Sandusky, Michigan). *Vice-Chairman:* W. D. Wilson (R. T. Vanderbilt Co., Detroit). *Secretary-Treasurer:* P. V. Millard (Automotive Rubber Co., Detroit). *Directors:* J. F. Stiff, J. M. Clark, Jack Masden, A. F. Thompson, Frank G. Falvey, R. W. Malcolmson, C. H. Albers, R. Huizinga, E. P. Francis, J. J. Fleming, R. C. Chilton, S. M. Sidwell, R. H. Snyder, R. C. Waters, E. W. Tillitson, T. W. Halloran. *Councilors:* H. F. Jacober, H. W. Hoerauf, J. T. O'Reilly. Meetings in 1959: April 18, June 26, October 2, December 2.

Fort Wayne Rubber Group

Chairman: Walton D. Wilson (R. T. Vanderbilt Co., 5272 Doherty Dr., Orchard Lake, Michigan). *Vice-Chairman:* A. Bluestein (Anaconda Wire & Cable Co., Marion, Ind.) *Secretary-Treasurer:* A. L. Robinson. *Directors:* M. J. O'Connor, Norman Klemp, E. Theall, H. Cantwell, H. Glassford, J. Lawless, R. Hartman, S. Choate, E. Bosworth. Meetings in 1959: June 5 (outing) ,September 24.

Los Angeles Rubber Group

Chairman: Charles H. Kuhn (Master Processing Corp., Lynwood). *Assoc. Chairman:* B. R. Snyder (R. T. Vanderbilt Co., Los Angeles). *Vice-Chairman:* W. M. Anderson. *Secretary:* C. M. Churchill (Naugatuck Chemical, East Los Angeles). *Asst. Secretary:* Edmund J. Lynch (H. M. Royal, Inc., Downey, Calif.). *Treasurer:* Howard R. Fisher (W. J. Voit Rubber Co., Los Angeles). *Directors:* Roy N. Phelan (Atlas Sponge Rubber Co., Monrovia), William J. Haney (Kirkhill Rubber Co., Brea), John L. Ryan (Shell Chemical Corp, Torrance), Carl E. Huxley (Enjay Co., Los Angeles), Walter E. Boswell (Thiokol Chemical Corp.). Meetings in 1959: May 5, June 5, 6 and 7, October 6, November 3, December 11.

New York Rubber Group

Chairman: R. B. Carroll (R. E. Carroll, Inc., Trenton, N. J.). *Vice-Chairman:* E. S. Kern (R. T. Vanderbilt, 230 Park Ave., N. Y.). *Secretary-Treasurer:* R. G. Seaman (Rubber World, New York). Terms end December 31, 1959. Meetings in 1959: June 4, August 4, October 16, December 18.

Northern California Rubber Group

President: Drace "Kut" Kutnewsky (Burke Rubber Co., San Jose). *Vice-President:* Claude "Corky" Corkadel (Oliver Tire & Rubber Co., Oakland). *Treasurer:* Joe Mattson (Witco Chemical Co., San Francisco). *Secretary:* Ray Brown (Burke Rubber Co., San Jose). *Directors:* Keith Large, Roy Woodling. Meetings in 1959: September 10, October 8, November 5.

Philadelphia Rubber Group

Chairman: R. S. Graff (E. I. du Pont de Nemours & Co., Wilmington). *Vice-Chairman:* H. C. Remsberg (Carlisle Tire & Rubber, Carlilse, Pa.). *Secretary-Treasurer:* R. N. Hendrickson (Phillips Chemical Co., 2595 East State Street, Trenton, N. J.). *Executive Committee:* T. E. Farrell, R. N.

HENDRIKSEN, JAMES JONES, GEORGE N. MCNAMARA, J. R. MILLS, H. M. SELLERS, MERRILL SMITH. *National Dir.:* M. A. YOUKER (E. I. du Pont de Nemours & Co., Wilmington). Meetings in 1959: May 1, August 21, October 2, November 6.

RHODE ISLAND RUBBER GROUP

Chairman: H. W. DAY (E. I. du Pont de Nemours & Co., Boston). *Vice-Chairman:* HARRY L. EBERT (Firestone, Fall River, Mass.). *Secretary-Treasurer:* W. J. BLECHARCZYK. *Historian:* R. G. BOLKMAN (U. S. Rubber Co., Providence). *Executive Committee:* E. S. UHLIG, R. B. ROBITAILLE, J. M. VITALE, C. A. DAMICONE, G. E. ENSER. Meetings in 1959: June 12–14, November 5.

SOUTHERN RUBBER GROUP

Chairman: WARREN HALL (Phillips Chemical Co., 318 Water Street, Akron, Ohio). *Vice-Chairman:* E. H. RUCH (Firestone Tire and Rubber Co., Memphis, Tenn.). *Secretary:* E. STRUBE (E. I. du Pont de Nemours and Co., Atlanta, Ga.). *Treasurer:* R. C. WHITMORE (Better Monkey Grip Co., Dallas, Texas). Meetings in 1959: June 5 and 6 Colonial Inn, St. Petersburg, Fla. Oct. 23 and 24 Peabody Hotel, Memphis, Tenn.

WASHINGTON RUBBER GROUP

President: ROBERT STIEHLER (National Bureau of Standards). *Vice-President:* A. W. SLOAN (Atlantic Research, Alexandria, Va.). *Secretary:* GEORGE T. RICHEY (National Bureau of Standards). *Treasurer:* J. R. BRITT (B. F. Goodrich Co.). Meetings in 1959: April 6, May 4, Patomac Electric Power Co. Auditorium.

NEW BOOKS AND OTHER PUBLICATIONS

THE KINETICS OF VINYL POLYMERIZATION BY RADICAL MECHANISMS. By C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon. Published by Academic Press, Inc., 111 Fifth Avenue, New York 3, New York. 6×9 inches, 330 pages. Price $8.80.—The subject of radical-initiated vinyl polymerization, although largely developed in the past thirty years, exhibits one of the most satisfactory applications of chemical kinetics to the interpretation of chemical reactions. The results of this work have very many important technical and commercial applications. Furthermore we have here a scientific subject which is approaching, but has not quite reached, the well rounded beauty of the classical sciences.

Many fine treatments of this subject have appeared either as parts of books on polymer chemistry or on chemical kinetics. A few books, e.g., that of Burnett, are devoted exclusively to the mechanism and kinetics of polymer reactions.

This work by Bamford et al. will find a useful place in the library of polymer chemistry and chemical kinetics. It tries to steer an intermediate course between conciseness and comprehensiveness by the criterion of critical choice. The reviewer found places, e.g., the initiation rate, where he felt that the treatment was insufficiently comprehensive; in other situations, especially Chapter 7, he felt that the treatment was not sufficiently concise or simple. Yet the

over-all impression is very good and the book can be highly recommended for all interested in the subject. [Reviewed by Arthur Tobolsky in *Journal of the American Chemical Society.*]

NUMBER–AVERAGE MOLECULAR WEIGHTS. FUNDAMENTALS AND DETERMINATION. By Robert U. Bonnar, Martin Dimbat, and Fred H. Stross. Published by Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, New York. 6 × 9 inches, 310 pages. Price $7.50.—The use of molecular weight determinations has become far more general since industrial and governmental research have assumed their present intense activity than it was in the days when research was restricted to educational institutions. In the control of industrial processes, the molecular weight determinations are now much used to obtain an estimate of degree of polymerization, in the thermodynamic calculations made for design of industrial processes and equipment, and to characterize fractions of separation processes. In such industrial applications, the time and labor required for the determination is of considerably greater importance than in academic research. Since this book is a product of industrial research, more space is given, in the discussion of competitive methods, to that method which is more rapid and less laborious without significant loss in accuracy. In some cases, as with the ebullioscopic methods, it has been possible to couple speed of analysis with an extraordinary sensitivity of the apparatus, and to improve repeatability as well as sample size requirement. Thus it is possible through use of multiple ebulliometers to reduce the time per sample to about one half of a man-hour, with samples as small as 0.01 g. Data can be obtained within a few hours from sampling.

A reasonable number of representative methods of more academic interest have also been described. Although some of these may be considerably more cumbersome and time consuming, the nature of the sample may require use of these methods.

To facilitate the choice of the method appropriate to the specific case, the first chapter gives a survey and summary of the methods described in the book. Each subsequent chapter discusses the individual classes of methods as outlined in the first chapter, with the exception of Chapter IV. Chapter IV provides some of the theoretical background, computation methods, and error theory applicable to the cryoscopic and ebullioscopic methods covered in Chapters II and III. Study of Chapter IV is suggested specifically to those who wish to develop fully the potentialities of the methods in question. For making determinations on samples where association, hydrogen-bonding, viscosity, unusual solution behavior, and similar effects do not constitute specific problems, the discussions in Chapters II and III will in most cases be sufficient.

A word also about the class of methods treated in this book. The number-average molecular weight of a mixture is the molecular weight computed by averaging the molecular weights of the individual mole fractions which are homogeneous with respect to this characteristic. Weight-average methods such as light scattering, are not treated, nor are the viscosity-average, nor the weight-weight, and *z*-average methods of the ultracentrifuge. The distinction becomes important with *analysands* of wide molecular weight range; the number-averaging process gives emphasis to the low values, and is consequently sensitive to low molecular weight impurities, such as monomeric and other low molecular contaminants in polymeric mixtures. The weight average has analogous features with respect to the high molecular constituents. It is seen, therefore, that comparison of results obtained by number-averaging and

weight-averaging procedures will furnish a measure of molecular weight distribution.

Single compounds of known composition that can be used as calibration standards are available at present only in the range below a molecular weight of 500. However, the determinations made by several averaging methods on a number of narrowly fractionated high molecular weight polymers have been reported recently and show such agreement that confidence in the accuracy of all methods involved now rests on a substantial basis. [Extracted from the preface of the book.]

EFFECTS OF RADIATION ON MATERIALS. Edited by J. J. Harwood, Henry H. Hauser, J. G. Morse, and W. G. Rauch. Published by Reinhold Publishing Corp., 430 Park Avenue, New York 22, New York. $6\frac{1}{4} \times 9\frac{1}{4}$ inches, 356 pages. Price $10.50.—Twelve papers presented at a colloquium at Johns Hopkins University jointly by the Office of Naval Research and the Martin Company are reproduced in this volume. Brought about by the need for greater understanding of the effects of radiation on materials, the program was designed to appeal to research scientists and engineers, as well as to manufacturers concerned with products for use in radiation fields. The papers deal with various materials affected by radiation, including organic and polymeric ones; theories and concepts of radiation effects; radiation sources and measurements of radiation, and known effects of radiation on the physical, metallurgical, mechanical, corrosion and electrical properties of the various materials. In addition, there is a discussion of current thinking on various reaction processes, e.g., graft polymerization.

Two of the papers, besides those dealing with the theoretical or basic information, are of particular interest to the rubber industry: "Effects of Radiation on Behavior and Properties of Polymers", by A. Charlesby, and "Radiation-Induced Graft Polymerization", by A. J. Restaino. Both of these papers, in keeping with the character of the symposium, give basic but detailed explanations and data of value to both the technician and the person with an academic interest in what happens to a polymer under the influence of radiation. The timeliness of the publication and importance of the subject should gain more than passing interest for this volume. Each paper is concluded with a list of literature references, and an appendix bibliography of 779 references is given at the end of the volume. A subject index is also provided. [Reviewed in *Rubber Age* (N. Y.).]

VISCOELASTIC BEHAVIOR OF RUBBER-LIKE HIGH POLYMERS. Parts I–V. By P. Ször. Published in *Acta Chimica Academiae Scientiarum Hungaricae*, Volume 8, pages 57–74, 75–96, 97–102, 103–114, 115–132 (1955).—The parts have the following sub-titles: I. The Alfrey-Theory of the Distribution of Retardation Times with Special Consideration of the Empirical Formula $\log \eta - \sqrt{M}$ and Its Correlation with deformation at Constant Stress; II. Deformation of Raw Rubber under Constant Stress as Function of Time; III. Superposition Principle; IV. Deformation of Vulcanized Rubber under Constant Stress as Function of Time; V. Derivation of the Distribution of Retardation Times on the Basis of the Empirical Linear Relation between $\log \eta$ and $\log M$ and its Connection with Deformation at Constant Stress. One copy of each (in English) is available at the Rubber Division Library, University of Akron, Akron 4, Ohio, for Thermofax duplication at a price of 10¢ per page.

PROGRAM OF THE GORDON RESEARCH CONFERENCES

15 June-4 September 1959

W. George Parks, *Director*

University of Rhode Island, Kingston, Rhode Island

The Gordon Research Conferences for 1959 will be held from 15 June to 4 September at Colby Junior College, New London, New Hampshire; New Hampton School, New Hampton, New Hampshire, and Kimball Union Academy, Meriden, New Hampshire.

Purpose. The conferences were established to stimulate research in universities, research foundations and industrial laboratories. This purpose is achieved by an informal type of meeting consisting of scheduled lectures and discussion groups. Sufficient time is available to stimulate informal discussions among the members of a conference. Meetings are held in the morning and in the evening, Monday through Friday, with the exception of Friday evening. The afternoons are available for recreation, reading or participation in discussion groups as the individual desires. This type of meeting is a valuable means of disseminating information and ideas to an extent that could not be achieved through the usual channels of publication and presentation at scientific meetings. In addition, scientists in related fields become acquainted, and valuable associations are formed that often result in collaboration and cooperative efforts between different laboratories.

It is hoped that each conference will extend the frontiers of science by fostering a free and informal exchange of ideas among persons actively interested in the subjects under discussion. The purpose of the program is not to review the known fields of chemistry and physics but primarily to bring experts up to date on the latest developments, to analyze the significance of these developments, and to provoke suggestions concerning the underlying theories and profitable methods of approach for making new progress.

In order to protect individual rights and to promote discussion, it is an established requirement of each conference that no part of the information presented is to be used without specific authorization of the individual making the contribution, whether in formal presentation or in discussion. Scientific publications are not prepared as emanating from the conferences.

Registration and Reservations. Attendance at the Conferences is by application. Individuals interested in attending the conferences are requested to send their applications to the Director at least two months prior to the date of the Conference. *All applications must be submitted on the standard application form which may be obtained by writing to the office of the Director.* This procedure is important because certain specific information is required in order that a fair and equitable decision on the application may be made. Attendance at each Conference is limited to approximately 100 individuals.

The director will submit the names of those requesting authorization to attend to the Conference Committee for each conference. This committee will review the names and select the members in an effort to distribute the attendance as widely as possible among the various institutions and laboratories represented. A registration card will be mailed to those selected as soon as possible. Advance registration by mail for each conference is required and registration is completed on receipt of the card and a deposit of $15. (Checks are to be made payable to the Gordon Research Conferences.) The deposit

of $15 will be credited against the fixed fee for the Conference if the individual attends the Conference for which he has applied. A registration card not accompanied by the $15 deposit will not be accepted.

The Board of Trustees of the Conferences has established a fixed fee of $100 for attendance at each Conference. This fee was established to encourage attendance for the entire Conference and to increase the Special Fund that is available to each Conference Chairman for the purpose of assisting conferees who attend a Conference at total or partial personal expense with their travel or subsistence expenses or with both. This fixed fee will be charged regardless of the time a conferee attends the Conference—that is, for periods of from one to four and one-half days. It is divided as follows: registration fee $40 ($15 for administration and $25 for the Special Fund); room and meals $60 (including gratuities), for five days. An additional charge of $1 per night per person will be made for a room with private bath or for a single room of which there are a limited number available. These rooms will be assigned in the order that applications are received.

Members attending a Conference are expected to live at the Conference location because one of the objectives of the Conferences is to provide a place where scientists can get together informally for discussion. It is to the advantage of all participants to attend a Conference for the entire week. If special circumstances warrant living elsewhere a registration fee of $50 is charged.

The fixed fee will cover registration, room (except room with private bath or single room), meals and gratuities. It will not provide for golf, telephone, taxi, laundry, conference photograph, or any other personal expenses.

Conferees living at the Conference location who will pay all or part of the fixed fee as a personal expense may request a reduction of $25 (special fund) in the fixed fee. Application for this special fee ($75) must be made when the registration card is returned to the Director.

Accommodations are available for a limited number of women to attend each conference, and also for wives who wish to accompany their husbands. All such requests should be made at the time the attendance application is submitted because these accommodations, limited in number, will be assigned in the order that specific requests are received. Children under 12 years of age cannot be accommodated. Dogs or other animals will not be permitted in the dormitories.

Special Fund. A special fund is provided for by the Board of Trustees from the registration fee and is made available to the chairman of each conference for the purpose of assisting scientists who could not otherwise attend or participate because of financial limitations. This fund is provided with the object of increasing the participation of research workers. Its use is not limited to scientists who have been invited by the chairman to attend a conference in order to present a paper. The money is to be used as an assistance fund only and may be used to contribute toward traveling expenses or subsistence expenses at the conference, or both. Total travel and subsistence expenses will not usually be provided.

Cancellations. The cancellation of an approved application for attendance at a conference will cause forfeiture of the $15 deposit.

Attendance. Requests for attendance at the conferences, or for additional information, should be addressed to W. George Parks, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. From 15

June to 4 September 1959 mail should be addressed to Colby Junior College, New London, New Hampshire.

The program on Elastomers is as follows:

PAUL G. CARPENTER, *Chairman*
ROBERT L. ZAPP, *Vice Chairman*

10 August

J. P. BUCKLEY and M. BERBER. A New Technique for Measuring Volume Swell and Its Application to Elastomer Studies.

A. R. KEMP. Solubility and Viscosity Characteristics of Elastomers.

R. NORMAN. Frictional Properties of Flexible Vinyl Polymers.

11 August

A. M. GESSLER. The Attrition of Carbon Black: Surface Chemistry and Reinforcing Effects.

E. M. DANNENBURG. Properties of Attrited Carbon Black.

E. R. BARTHOLOMEW. Elastomers for High Temperature Services.

12 August

R. D. STIEHLER. Observations on Tire Performance.

A. D. DINGLE et al. Resilience and Power Loss of Elastomers.

Speaker and Subject to be announced.

13 August

C. F. FRYLING. Colloidal Properties of Synthetic Latexes.

Speakers and Subjects to be announced.

14 August

OLIVER BURKE and ELDON STAHLEY. Vinylic Filler Reinforcement of Elastomers.

THE REACTIONS OF ISOCYANATES AND ISOCYANATE DERIVATIVES AT ELEVATED TEMPERATURES *

J. H. SAUNDERS

MOBAY CHEMICAL COMPANY, NEW MARTINSVILLE, W. VA.

I. INTRODUCTION

The reactions of isocyanates at moderate temperatures have been reviewed many times[1,17] and are generally well known. The reactions at elevated temperatures may be somewhat less familiar, and are often complicated by subsequent reactions of and with the initial reaction products. This review attempts to present the most essential reactions which may be expected of three commercially significant structural groups, isocyanate, urea and urethane, at temperatures in the approximate range of 100–300° C.

The reactions surveyed here are of great importance in designing polyurethane and polyurea structures which will have maximum temperature resistance, and in understanding changes which may take place at elevated temperatures. It is noteworthy that certain of the reactions presented here lead to breaking of chains, others result in increased crosslinking, while still others provide neither chain scission nor changes in crosslinking. The success to which these reactions have been adapted to polymer chemistry may be illustrated by the existence of flexible urethane foams which show very little change in load bearing strength after fifteen months at 100° C, urethane elastomers which may be used for short times to temperatures of 130–150°, an experimental one pound per cubic foot rigid urethane foam which is dimensionally stable for five days at 200°, and a urethane wire enamel which retains adequate electrical and physical properties after aging for several thousand hours at 180° or one hundred hours at 250° C.

II. ISOCYANATE REACTIONS

A. WITH ACTIVE HYDROGEN COMPOUNDS

At low or moderate temperatures the reactions of isocyanates are usually relatively simple, normally involving addition of an active hydrogen compound to the nitrogen-carbon double bond. Such a reaction is the familiar formation of a urethane from an isocyanate and an alcohol:

$$RNCO + R'OH \longrightarrow RNHC(=O)OR'$$

At temperatures close to 100° C and above similar reactions may also occur. In addition to the relatively reactive amines, alcohols, carboxylic acids and water, less reactive compounds such as ureas, urethanes and amides may add

* An original publication.

to the isocyanate at elevated temperatures[5,11,13,14]:

$$\text{RNCO} + \text{R'NHCONHR'} \longrightarrow \text{RHNCONCONHR'}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{R'}$$

a urea — a biuret

$$\text{RNCO} + \text{R'NHCOR''} \longrightarrow \text{RNHCONCOR''}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{R'}$$

an amide — an acylurea

$$\text{RNCO} + \text{R'NHCOOR''} \longrightarrow \text{RNHCONCOOR''}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{R'}$$

a urethane — an allophanate

It is readily noted that these reactions are actually the combination of isocyanate with initial reaction products from isocyanates and amines, carboxylic acids and alcohols, respectively. Furthermore, the active hydrogen has still not disappeared. Thus it is probable that several moles of isocyanate can be consumed by only one mole of an active hydrogen compound. Such a sequence of reactions may be important with regard to distillation losses during isocyanate production.

$$\text{R'NCO} + \text{RNHCONHR} \longrightarrow \text{R'NHCONCONHR}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{R}$$

$$\xrightarrow{\text{R'NCO}} \text{R'NHCONCONCONHR}$$
$$\qquad\qquad\qquad\qquad\quad | \quad |$$
$$\qquad\qquad\qquad\qquad\quad \text{R'} \quad \text{R}$$

Fortunately the rates of reactions of isocyanates with active hydrogen compounds are sufficiently different that one can usually suppress the subsequent reactions with the initial products, if desired. Thus amines react readily even at 0°, while alcohols, water and some carboxylic acids react at moderate rates at 25–50°. Reactions with other carboxylic acids, ureas, amides and urethanes may become important at about 100° and above, with the relative reactivity usually decreasing approximately in the order given.

Recent data on the relative reactivities of a series of active hydrogen compounds as given by Morton and Deisz[14] are shown in Table I. (Experience in our laboratory indicates that in certain other systems the relative rates of reaction of isocyanate with water and with primary alcohols are more nearly equal than is indicated in Table I.)

Qualitatively similar data on the rates of reactions of monoisocyanates with substituted ureas and urethanes are given[5] in Table II. In this study the reactions with substituted ureas followed second order kinetics, but the reactions

TABLE I

RELATIVE RATES[14] OF REACTIONS, PHENYL ISOCYANATE AND ACTIVE HYDROGEN COMPOUNDS, 80° C

Active hydrogen compound	$K \times 10^4$ l/mole sec	Relative rate
n-Butyl phenyl carbamate	0.06	1
Acetanilide	0.99	16
n-Butyric acid	1.56	26
Diphenylurea	4.78	80
Water	5.89	98
n-Butanol	27.5	460

TABLE II

RELATIVE RATES[5] OF REACTIONS, AROMATIC ISOCYANATES AND SUBSTITUTED UREAS AND URETHANES

(Approximately 0.01 molar in each reactant, in dichlorobenzene)

Isocyanate	Urea	Urethane	Temp. ° C	$K \times 10^4$, l/mole sec
Phenyl	$C_6H_5NHCONH_2$	—	60	3.7
Phenyl	$C_6H_5NHCONH_2$	—	100	32.
Phenyl	$C_6H_5NHCONH_2$	—	140	48.
Phenyl	$(C_6H_5NH)_2CO$	—	100	9.9
Phenyl	$(C_6H_5NH)_2CO$	—	140	23.
Phenyl	—	$C_6H_5NHCOOC_2H_5$	140	0.2 (0.14*)
o-Tolyl	$C_6H_5NHCONH_2$	—	100	11.
o-Tolyl	$C_6H_5NHCONH_2$	—	140	18. (21*)
o-Tolyl	$(C_6H_5NH)_2CO$	—	100	3.6
o-Tolyl	$(C_6H_5NH)_2CO$	—	140	8.2 (3.8*)
o-Tolyl	—	$C_6H_5NHCOOC_2H_5$	140	0.1

* With ethyl morpholine, 10% based on isocyanate concentration.

with urethanes did not. Calculated rate constants for the reactions with urethanes decreased with time; the data did not give good agreement with any rate equation used. For comparison purposes, calculated second order rate constants for approximately the 5–10 per cent reaction range are given in Table II.

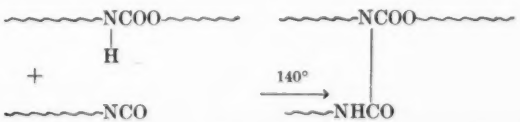
The reactions of aryl isocyanates with substituted urethanes without solvent were also studied by Kogon[12], who found that an equilibrium was obtained.

$$RNCO + R'NHCOOR'' \rightleftharpoons RNHCONCOOR''$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad R'$$

Good agreement with second order rate calculations was reported, with rate constants ($K \times 10^4$, l/mole sec) in the range of 0.017 at 160° to 0.065 at 137° for phenyl isocyanate and ethyl carbanilate. Equilibrium constants (l/mole) were 0.397 at 106° and 0.203 at 137°. Rate and equilibrium constants, energies of activation, heat of reaction and entropy of reaction were reported for several combinations of isocyanates and substituted urethanes. Methyl morpholine had no significant effect on the rate of reaction.

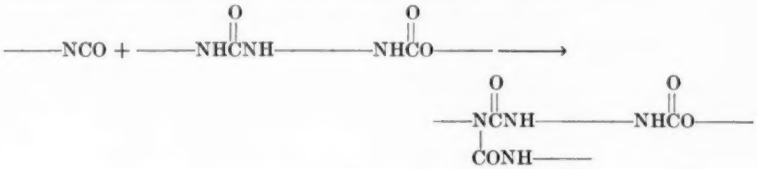
All rate studies in dilute solutions should be used with caution when translating to reactions occurring in non-solvent systems. The relative rates which obtain during the formation of an elastomer or a foam may conceivably be quite different from those observed in solution studies.

The reactions of isocyanates with substituted ureas, urethanes, and amides are particularly important in polyurethane chemistry because if permitted to occur they will lead to increased branching. Thus a linear polyurethane prepared from a diol and a diisocyanate may be branched by allophanate formation:



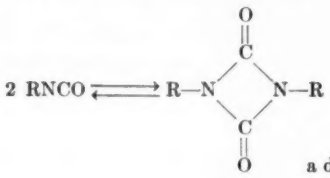
Because of the faster relative rate of reaction of isocyanate with urea groups, a polymer containing both urea and urethane groups in approximately equal

concentrations may be branched principally by biuret formation:

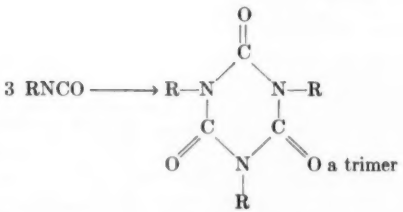


B. SELF CONDENSATION

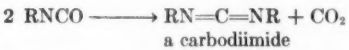
In addition to the simple reactions, other isocyanate reactions which do not normally occur to a significant extent at room temperature may also take place at elevated temperatures. These are the self condensation reactions, dimerization[2,3], trimerization[2] and carbodiimide formation[9]:



a dimer



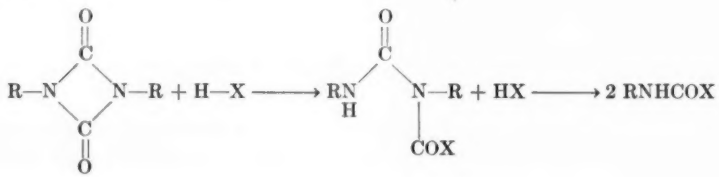
a trimer



a carbodiimide

Dimerization proceeds most readily when there are no shielding groups *ortho* to the isocyanate group. Thus the 4-position NCO group of 2,4-tolylene diisocyanate dimerizes much faster than the 2-position group.

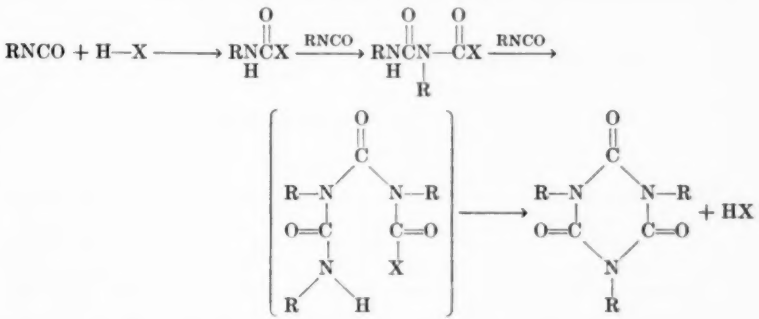
Dimerization may be the least important of these since the dimer itself does not have great thermal stability. Above about 150° many dimers dissociate to the monomers. Dimers also are reactive toward amines at moderate temperatures, e.g., 50° C and higher, and toward hydroxy compounds at higher temperatures[3,16].



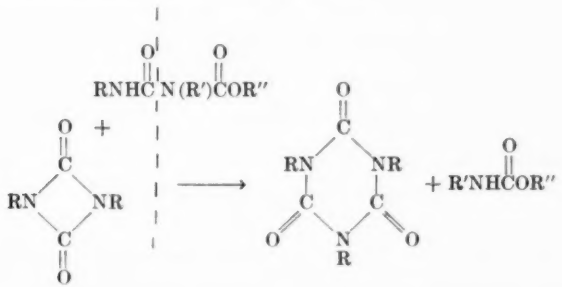
Simple heating of certain dimers has converted them to the corresponding trimers, possibly through regeneration of the monomer and subsequent trimerization.

Trimerization is an important reaction in that the trimer is relatively quite stable in the range of 150–200°. In addition, in polyurethane chemistry, trimerization is significant because it leads to branching of the polymer. Similar to dimerization, the presence of *ortho* substituents greatly reduces the tendency to trimerize.

It is possible that trimerization proceeds most readily in the presence of at least trace amounts of some active hydrogen compound:



Kogon[11] has shown that a mechanism involving the dimer and an allophanate as intermediates obtains under certain conditions.



Such a mechanism may be similar to the last step of the more general, qualitative suggestion, where the HX eliminated is the urethane.

An example of a polymer decomposition which apparently resulted in trimerization was reported by Swerdloff and McFarlane[18]. Heating a polyurethane from tetramethylene diisocyanate and 1,4-butanediol at 240–250° produced five products: tetrahydrofuran, a low molecular weight polyurethane, a low molecular weight polyurea, $H_3N^+(CH_2)_4NHCONH(CH_2)_4NHCO_2^-$, and a polymer having the elemental analysis of tetramethylene diisocyanate and assumed to be a polymer formed by trimerizing the isocyanate groups.

Carbodiimides may be one of the ultimate decomposition products of isocyanates. The formation of the carbodiimide normally requires a very high

temperature (180–300°). It is noteworthy in polymer applications that carbodiimide formation does not change the degree of branching of the polymers.

Polymeric carbodiimides have been obtained by heating the bis-neopentyl urethane of diphenylmethane diisocyanate[9]:

$$CH_2[C_6H_4NHCOOCH_2C(CH_3)_3]_2 \xrightarrow{300°} \begin{matrix} CO_2 & 45\% \\ ROH & 91\% \\ \text{polymer} & 98\% \end{matrix}$$

The polymer thus obtained showed an infrared absorption at 4.7–4.8μ, indicating the carbodiimide structure, —N=C=N—. Similarly, heating the isocyanate itself at 300° gave a polymeric carbodiimide[9]:

$$CH_2(C_6H_4NCO)_2 \xrightarrow[45\text{ min}]{300°} \underset{92\%}{[N{=}C{=}N{-}C_6H_4CH_2C_6H_4]_n} + CO_2$$

III. REACTIONS OF ISOCYANATE DERIVATIVES

A. URETHANES

The stability of urethanes varies greatly, depending on the structure of the urethane. Urethanes from tertiary alcohols decompose readily at temperatures as low as 50° C, whereas urethanes from many primary and secondary alcohols may undergo changes only slowly at 150–200°. The environment, i.e., presence of other reactants and catalysts, also greatly influences the stability of the urethanes.

Studies of the thermal decomposition of substituted urethanes have shown that three general types of reactions may take place[6,9,13,15,18]:

1. Dissociation to Isocyanate and Alcohol:

$$RNHCOOR' \rightleftharpoons RNCO + R'OH$$

2. Formation of Primary Amine and Olefin:

$$RNHCOOCH_2CHR' \longrightarrow RNH_2 + CO_2 + R'CH{=}CH_2$$

3. Formation of Secondary Amine:

$$RNHCOOR' \longrightarrow \underset{H}{RNR'} + CO_2$$

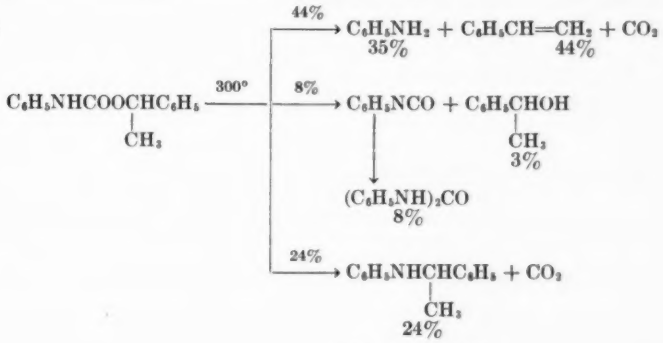
Under the proper conditions the dissociation of a urethane has been used to prepared isocyanates in good yield. In the special case where the urethane of a phenol is used the dissociation may occur at temperatures as low as 150°. The following example illustrates a typical dissociation[9]:

$$C_6H_5NHCOOC_2H_5 \xrightarrow[2\text{ hr}]{200°\text{ C}} \underset{71\text{–}74\%}{C_6H_5NCO} + \underset{90\text{–}92\%}{C_2H_5OH}$$

The decomposition of a urethane to the primary amine and olefin is favored in cases where the corresponding alcohol is readily dehydrated. Urethane formation and subsequent decomposition have been used to dehydrate certain alcohols, e.g., tertiary alcohols in good yields. This type of reaction may also occur to some extent with urethanes of primary and secondary alcohols at 200–

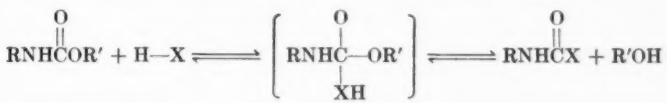
250°. In polyurethane decompositions this reaction would cause rupture of the polymer chains.

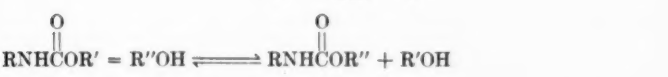
An example of urethane decomposition with olefin and secondary amine formation was reported by Dyer, Newborn and Wright[9]:



Total CO_2: 84%

In addition to the three decomposition reactions, urethanes may undergo reaction with a variety of reagents which will add to a carbonyl group. It is reasonable to assume that dissociation to the isocyanate is not required, but that reaction may occur analogous to transesterification type reactions[13,15]:





The ease of displacement of OR′ apparently is greater for aryloxy groups than for alkoxy groups. Equilibria seem to favor urea formation more than O-aliphatic urethane, which in turn is favored more than O-aryl urethanes.

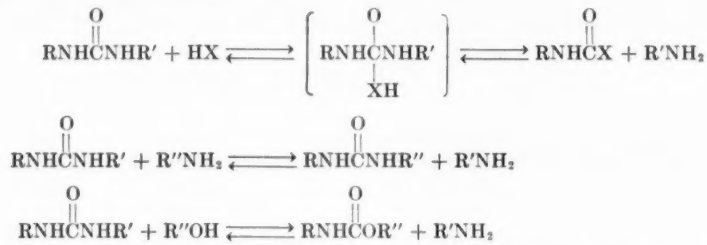
B. UREAS

Substituted ureas are known to dissociate to the corresponding isocyanate and amine at elevated temperatures:

$$RNHCONHR' \rightleftharpoons RNCO + RNH_2$$

Vapor density measurements have shown diphenylurea to be 99 per cent dissociated at 370°. Also when HCl was added to prevent recombination of the isocyanate and amine, yields of isocyanate up to 71 per cent have been obtained, with nearly quantitative recovery of the amine salt[4].

In reactions analogous to those of the urethanes, ureas may undergo typical carbonyl addition reactions[10,13,15]:



Ureas have been shown to interact with each other in a manner called "dearrangement"[7,8]:

Such a reaction may be assumed to involve dissociation to the amines and isocyanates, followed by random recombination, and attack of free amine on urea molecules.

Diarylureas seem to be among the most favored reaction products in all reactions of aryl isocyanates at elevated temperatures. The formation of diphenyl urea (carbanilide) has dominated many reactions of phenyl isocyanate, e.g., that with ethyl urethane at 175°[13].

IV. CATALYSIS

Tertiary amines are among the most commonly used catalysts for promotion of those isocyanate reactions which occur at moderate temperatures, i.e., reactions with alcohols, carboxylic acids and water. In contrast, however, the tertiary amines are not usually very potent catalysts for the reactions with active hydrogen compounds discussed in this survey. For example, in rate studies ethylmorpholine had no apparent catalytic effect on the reaction between phenyl isocyanate and ethyl carbanilate, as well as reactions between *o*-tolyl isocyanate and phenyl urea and diphenylurea at 140° in dilute solution. Similarly, tertiary amines have only a mild effect on the dry storage life of prepolymers containing urethane, isocyanate and some urea groups. On the other hand, at least certain tertiary amines do catalyse dimerization at 25–50°, and in the presence of simple urethanes catalyse trimerization.

Catalysts which may have a very vigorous effect on some or all of the reactions discussed in this survey are the strong bases, e.g., NaOH, NaOR, and R_4NOH, and metal catalysts, e.g., cobalt naphthenate. Careful studies have not been made to completely illucidate the role of these catalysts and show which specific reactions they promote. However it is well known that they may promote one or more of the various reactions leading to crosslinking and gas evolution. For example if one attempts to prepare a prepolymer under conditions such that the over-all system is alkaline because of a strong base, e.g., Na_3PO_4, the prepolymer will gel, often with the evolution of gas.

If one wished to catalyse the reactions discussed here he would normally prefer to combine a mild catalyst, e.g., a tertiary amine, and an elevated temperature to provide adequate control of the operation. The use of a strong

base, e.g., NaOR, would permit reaction at a lower temperature, but many of the reactions might easily become uncontrollable. Reactions of explosive violence have been known to occur when less than 1 per cent of KOH was used as a catalyst.

V. CONCLUSIONS

Qualitative and quantitative studies with model compounds have shown that a variety of reactions may occur at 100–300° in molecules containing isocyanate, urea and urethane groups. All or most of these reactions are subject to catalysis so that they may be induced to proceed at lower temperatures. These reactions are quite important as they may affect the production and practical use of polyurethanes and polyureas.

By the proper selection of reaction components one may design a polyurethane or polyurea molecule which will give both a reasonable rate of cure to the final state and a degree of temperature stability suitable for many rigorous applications. The choice of reactive groups providing approximately the desired rates of reaction and of suitable catalysts may be used to achieve the necessary curing rate. The initial choice of a catalyst which will have a minimum effect on decomposition reactions, or the removal of the catalyst from the cured polymer will favor polymer stability. A selection of reactants which will minimize those decomposition reactions leading to chain rupture, and which will compensate for what rupture may occur, will promote polymer stability. Simple illustrations of such choices would include eliminating tertiary aliphatic hydroxyl groups from the hydroxyl-bearing component and including some degree of branching commensurate with the degree of elasticity or rigidity desired. Branching should be achieved through the more stable groups, e.g., urethane, urea or trimer, rather than through the less stable allophanate and biuret groups.

Many thoroughly tested applications of polyurethanes and mixed polyurea-urethanes show that it is readily possible to produce such polymers with excellent thermal stability.

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QUANTITATIVE MEASUREMENT OF RATE OF OZONE CRACKING *

A. G. VEITH

B. F. GOODRICH RESEARCH CENTER, BRECKSVILLE, OHIO

The problem of ozone attack on unsaturated rubbers has been recognized for some time but quantitative studies of this problem have only recently appeared in the literature. This is in great part due to the intractable nature of the phenomenon in regard to measuring the extent of cracking. In recent years several workers have been active in this field. Shaw and Adams[1] employed both electrical resistivity and creep under intermittent load to measure the attack of ozone. Rugg[2] used a microscopic technique to measure crack depth. Gable and Leeper[3] reported on the effect of a series of antiozonants on continuous creep in ozone. Buckley and Robinson[4] described a technique for determining the short-range creep of butyl rubber in ozone with a strain gage apparatus. Earlier Newton[5] and Crabtree and Kemp[6] contributed to an understanding of the action of ozone on rubbers.

The work to be described in this report covers two main points (*a*) securing a controlled ozone atmosphere in which to carry out tests and (*b*) a description of some of the preliminary results of a program intended to provide basic information on the phenomenon of ozone cracking.

CONTROLLED OZONE ATMOSPHERE

The present ASTM procedure for assessing the resistance of rubber to ozone cracking is Tentative Method of Test for Accelerated Ozone Cracking of Vulcanized Rubber (D 1149-55T), 1955 Book of ASTM Standards, Part 6, p. 1162. The ozone test chamber specified for testing is that described by Crabtree and Kemp[6]. This chamber does not provide for adequate forced circulation of the ozonized air, and the rate of movement of ozonized air through the chamber is too low to maintain constant ozone concentration without stratification. Those concerned with ozone testing recognize the deficiencies of this chamber and attempts have been made to correct the situation. Development work in our laboratories under the direction of J. R. Beatty was begun several years ago to construct a chamber that would provide rapid circulation and a high rate of air throughout. Two such chambers have been built. Figure 1 is a photograph of the latest of these two chambers. This chamber is larger than most commercial ones, with an internal volume of 0.38 cu m (13.4 cu ft). Flow rates of up to 12 cu m per hr (7 cu ft per min) can be maintained. Due to very efficient circulation by a fan placed at the top of the chamber, flow rates of 6 to 8 cu m per hr are entirely adequate at ordinary ozone levels. This chamber can be operated from room temperature to 150° F over an ozone concentration range of 10 to 700 parts per hundred million (pphm). A revolving test rack for mounting various types of samples is included.

* Reprinted from "Symposium on Effect of Ozone on Rubber", Special Technical Publication No. 229, American Society for Testing Materials, 1958, pages 97–112.

If the air throughput rate of a chamber drops below a certain level, the rubber responds to the action of ozone as though the concentration were lower than that measured by chemical analysis. This has been confirmed by running concurrent measurements of ozone concentration, one method using a B. F. Goodrich ozonometer[7], the other employing the usual chemical analysis. For this purpose the ozonometer had been calibrated at an air flow rate high enough to give deflection rates independent of flow rate but directly related to ozone concentration. As flow rate is reduced, a point is reached where the two

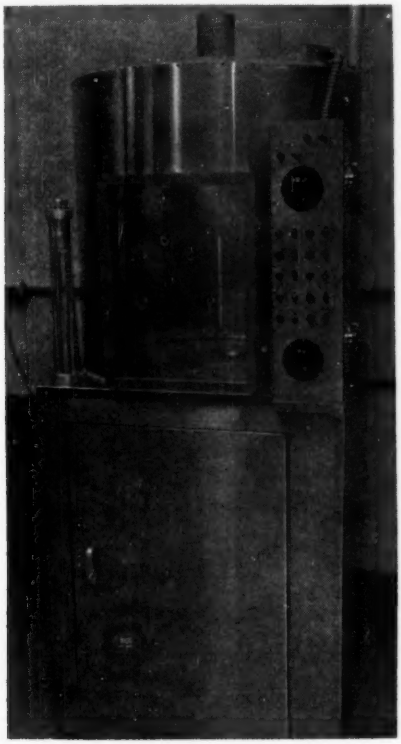

FIG. 1.—Ozone chamber.

methods do not give equivalent ozone concentrations. At this point and below, the concentration indicated by the ozonometer is lower than that determined chemically. The ozonometer depends upon the action of ozone on rubber, and therefore the rubber is not responding as the chemical analysis might indicate. This failure of the rubber thread, or sensitive element of the ozonometer to respond indicates that rubber test samples would behave similarly. The problem of overloading an ozone chamber with a large number of samples also falls into this general category. Analyses for ozone concentration should always be made with the chamber loaded if a meaningful value is sought. Both of the

above circumstances can be avoided to a large degree if the air flow through the chamber is maintained at a high rate.

A second deficiency of ASTM Tentative Method D 1149-55T and the Crabtree-Kemp chamber lies in the ozone analysis technique. The adjustment of the spray jet is often hard to control, and an empirical factor is included in the calculation of the ozone concentration. This empirical factor corrects for the loss of iodine by volatilization. The relatively high vacuum (about 60 cm mercury) over the iodine solution is mainly responsible for this loss. To circumvent both of these difficulties, a counter-current extraction column (Figure 2) has been devised to scrub ozone from an ozonized air stream. The carrier gas (air) containing ozone passes upward through a column packed with $\frac{1}{4}$-in.

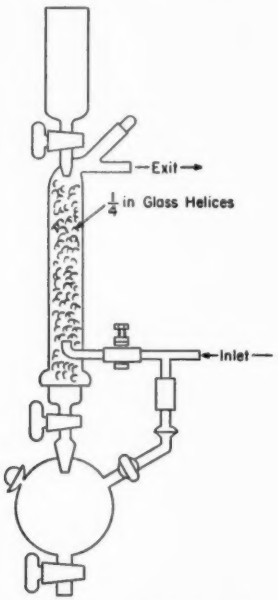

FIG. 2.—Counter-current ozone column.

glass helices. A buffered solution of potassium iodide percolates down through the column passing into a collection flask at the bottom. The wetting of the helices by the solution creates a large surface for absorption of the ozone. As the solution flows down the column, the dissolved iodine is carried into the collection flask. Tests have been conducted which show that the column removes all of the ozone from the stream at 0.3 cu m per hr flow rate up to 250 pphm, and it will probably do so as high as 500–700 pphm. No loss of iodine occurs in the operation of this column since the dissolved iodine is quickly carried out of the path of the air stream and the maximum pressure drop in the system is 5 to 10 mm of mercury due to the absence of a resistive element to the air flow such as the jet of the Crabtree-Kemp apparatus.

Figure 3 indicates in schematic form the arrangement of the ozone analysis

apparatus. The flow meter has been placed behind the absorption column, and glass tubing is used to convey the ozonized air from the chamber to the analysis equipment. The flow meter has been placed behind the absorption column to obtain a slightly more steady flow reading and to prevent any possible decomposition of ozone in the meter at high ozone levels. If no decomposition occurs in passing through the meter it may be placed either before or after the absorption column. In the Crabtree-Kemp (ASTM Tentative Method D 1149-55T) procedure, the meter must be placed ahead of the spray jet, since a high pressure drop occurs behind this jet, and a meter of this type is intended for use at near atmospheric pressures. A thermometer well and thermometer are placed after the dry ice trap to measure the temperature of the air stream prior to its entry into the flow meter. This temperature is used in calculating the ozone concentration. Normally this temperature is only slightly below ambient room temperature. A glass line is used to convey the ozonized air to the analysis apparatus. It has been observed that in some instances plastiziced poly (vinyl chloride) tubing may cause a partial decomposition of ozone. Short connecting sections used with glass tubing are not subject to this fault.

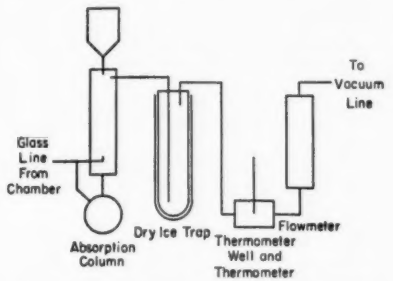

FIG. 3.—Arrangement of ozone analysis apparatus.

RATE OF OZONE ATTACK

For a fundamental study of the rate of ozone attack on rubbers, some quantitative method must be devised which is relatively simple in technique; yet the parameter to be measured must accurately reflect the condition of the sample at any time. Many methods have been proposed by various workers, some of which have been mentioned in the introductory remarks. It was decided after some preliminary experiments that the above requirements could be met by a measurement of creep under constant load.

Although there are two separate reports in the literature on the use of creep for assessing the damage due to ozone[1,3], neither of these goes beyond a superficial treatment of the method. The simplicity of the method warranted further detailed investigation on the effects of some simple variables and in particular to determine if the method was able to yield a measure of an "absolute" rate of attack or cracking. The word absolute is used in the sense that the rate is independent of the type or shape of specimen.

The expterimental technique for carrying out creep measurements is relatively simple. A special test rack was built to hold 12 separate specimens for creep in simple extension. Rectangular specimens are mounted in the clamps with soft asbestos pads to protect the ends from preferential attack. Figure 4

is a photograph of the test rack with 12 specimens in place. An overnight period in an ozone-free atmosphere reduces the creep due to viscoelastic behavior to a negligible rate. The samples are then inserted into a glass-fronted ozone chamber. Initial readings are quickly taken and the ozone-induced creep is followed by measuring the clamp separation with a cathetometer ac-

FIG. 4.—Creep test rack.

curate to ± 0.05 mm. The initial elongation is obtained by adding lead shot to the small bucket attached to each lower clamp. All measurements reported here were made at $90° \pm 2°$ F. The rubber formulations used are given in Table I.

The results reported here are of a preliminary nature. The variables studied are (*a*) effect of specimen geometry, (*b*) effect of initial elongation, and (*c*) the creep rate of some common commercial polymers or rubbers. It was deemed

TABLE I

FORMULATIONS USED

	Mix A	Mix B
Pale crepe	100	—
SBR (1502)	—	100
Zinc oxide	5	5
Stearic acid	2	2
MBT[a]	1	1.5
Sulfur	2.5	2

[a] Mercaptobenzothiazole.

necessary that something be learned about these variables, especially the first two, before proceeding to other problems such as the effect of antiozonants.

CREEP MEASUREMENTS IN GENERAL

When the length of a specimen is plotted as a function of time, curves similar to those of Figure 5 will be obtained. The extension ratio λ is plotted vs. the time of exposure in ozone. The quantity λ is the ratio of the extended length to the unextended length. The initial approach to obtaining a single parameter from such a curve was to use the slope of a straight line drawn through the points somewhat removed from the origin as a measure of the rate of ozone attack.

More extensive consideration of this technique soon indicated that a more detailed approach was needed. Since ozone in attacking rubber decreases the cross-sectional area, it seemed that the time variation of this parameter would be likely to give an authentic measure of ozone attack.

The kinetic theory of rubber elasticity describes the force-extension behavior of a gum rubber by means of the equation

$$f = 2AC(\lambda - \lambda^{-2}) \tag{1}$$

where f = tensile load, A = unloaded or original cross-sectional area, λ = the extension ratio and C = a constant which is a function of the state of cure. Equation (1) can be rearranged to give

$$A = \frac{f}{2C}\left(\frac{1}{(\lambda - \lambda)^{-2}}\right) \tag{2}$$

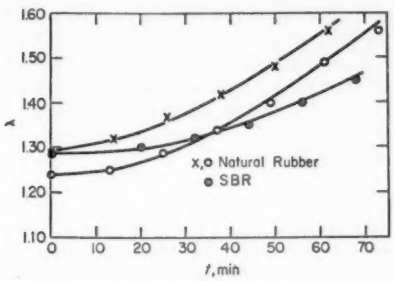

FIG. 5.—Plot of λ vs. time of exposure to ozone.

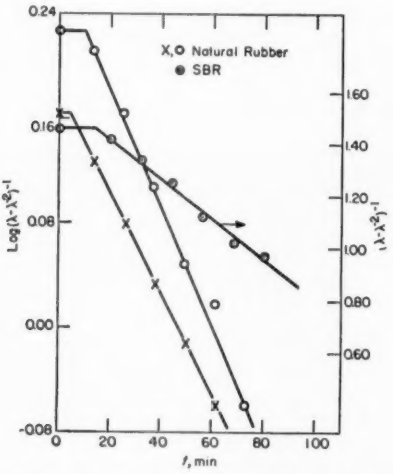

FIG. 6.—Plots of $(\lambda - \lambda^{-2})^{-1}$ vs. time. (*a*) Left ordinate: log $(\lambda - \lambda^{-2})^{-1}$ vs. time. (*b*) Right ordinate: $(\lambda - \lambda^{-2})^{-1}$ vs. time.

Under the conditions of the test, the load f is constant; therefore the term $f/2C$ is also constant for a given rubber. By plotting $(\lambda - \lambda^{-2})^{-1}$ as a function of time, the rate of change of A can be determined. Figure 6 shows a plot of log $(\lambda - \lambda^{-2})^{-1}$ vs. time for the natural gum rubbers shown in Figure 5. After a short period of induction, the initial decrease of log $(\lambda - \lambda^{-2})^{-1}$ is linear with time. This dependence on time indicates that the following equation describes the decrease in A for a natural vulcanized gum rubber:

$$A = A_0 e^{-kt} \tag{3}$$

where:

A = unelongated area at any time,
A_0 = original unelongated area, and
k = a constant.

The area A is an "average" unelongated area. The shape of the test specimen undergoing cracking is changing, that is, its cross-sectional area is decreasing. A plot such as Figure 6 measures this change. The are A at any time t is the average unelongated area that the specimen would have if the load were removed. It might be more correct to speak of A as the minimum area since the minimum area must necessarily affect the value of λ. Actually there is a distribution of cross-sectional areas along the specimen and the number, average and minimum will all influence λ. A must therefore be termed a special "average" area.

The plot for the SBR gum rubber gave a linear dependence for $(\lambda - \lambda^{-2})^{-1}$ vs. time. Later experiments indicated that under some circumstances log $(\lambda - \lambda^{-2})^{-1}$ vs. time was linear for this rubber. Such situations are resolved by using the initial rate of cross-sectional area decrease to assess the rate of attack by ozone.

The initial rate when a log

$$(\lambda - \lambda^{-2})^{-1}$$

dependence is found is

$$\left[\frac{dA}{dt}\right]_{t=0} = kA_0 \tag{4}$$

and when a linear dependence is found it is

$$\left[\frac{dA}{dt}\right]_{t=0} = K = \psi k_1 \tag{5}$$

In these equations, k is the slope of a plot of log $(\lambda - \lambda^{-2})^{-1}$ vs. t and K is equal to the slope of a $(\lambda - \lambda^{-2})^{-1}$ vs. t plot (k_1), multiplied by ψ where:

$$\psi = \frac{f}{2c} \tag{6}$$

The advantages for choosing the initial rate of cross-sectional area decrease will become evident in the ensuing discussion of results. Briefly, they are (*a*) extension ratio is known, (*b*) initial cross-sectional area is accurately known, (*c*) the initial rate can be used for polymers where the dependence of A on time is not identical, and (*d*) the constant C in Equation (1) is somewhat dependent on λ. For small changes in λ this is not serious, but for large changes it is. By restricting the measurements to the initial conditions this effect is minimized. In the discussion that follows the term rate or initial rate will be used to denote $\left[\frac{dA}{dt}\right]_{t=0}$.

There are two phenomena involved in the ozone cracking of rubber. These are crack formation and crack growth. Before proceeding to the effects of

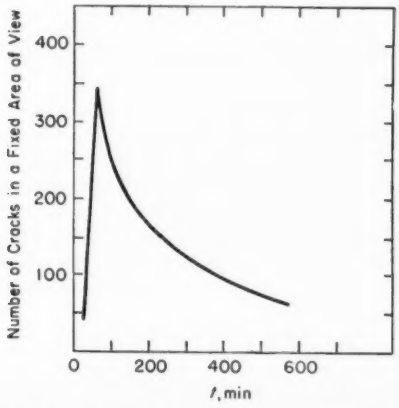

FIG. 7.—Crack density vs. time of exposure. Date from: Smith and Gough[8].

simple variables, an examination is necessary to determine the nature of the rate of cross-sectional area decrease and the induction period during which no creep occurs. Smith and Gough[8] have reported on both the formation and growth of ozone cracks in natural gum rubbers. Their results as well as experiments in these laboratories show that for unprotected natural rubber the formation of cracks is very rapid. Figure 7 is taken from the paper of Smith and Gough[8]. The number of cracks increases sharply and then declines. The decline is due to crack growth which results in crack coalescence. A measurable induction period precedes this rapid growth. Since no rapid increase in length followed by a decline in rate has ever been observed, the creep of a

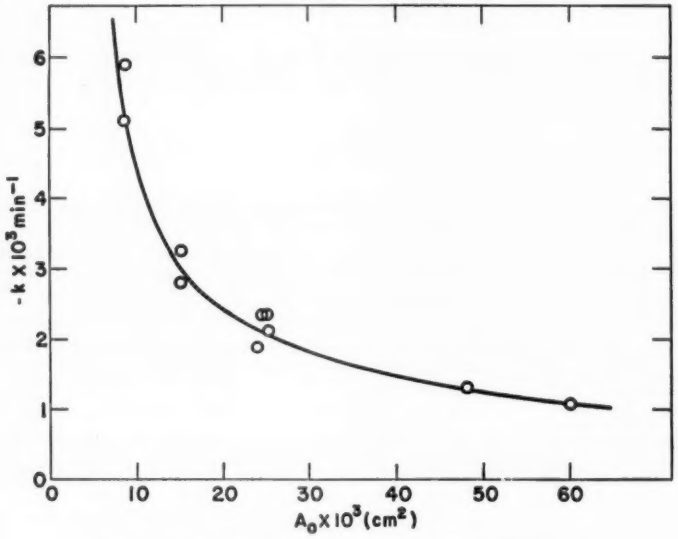

FIG. 8.—Plot of k vs. initial cross-sectional area A_0. Natural rubber.

specimen is primarily the result of the growth of ozone cracks. The end of the induction period, which is signalled by the first creep, is due to the formation of cracks of such size that their immediate growth causes detectable creep or cross-sectional reduction. Microscopic examination confirms this. Changes in cross-sectional area of the order of 2 per cent are capable of detection.

The technique therefore consists of measuring the rate of *collective* crack growth during the period of actual creep, and the induction period is a measure of the time necessary to form detectable or technically significant cracks.

GEOMETRY OF SPECIMEN

A series of measurements was carried out to determine the effect of specimen geometry. All test specimens were of rectangular shape. The "normal" specimens were 0.125 in. in width and 0.014 to 0.020 in. in thickness. Varia-

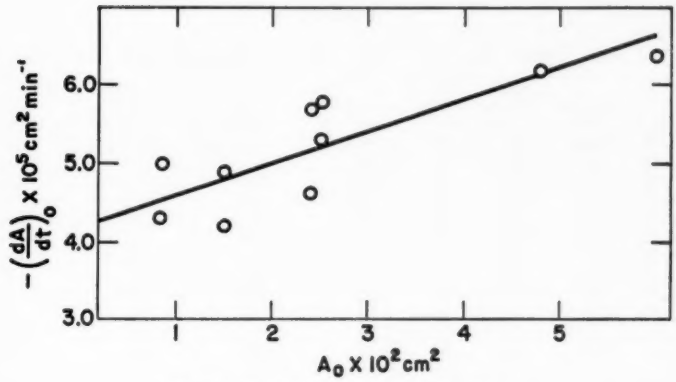

FIG. 9.—Plot of rate vs. A_0. Natural rubber.

tions including this "normal" sample were as follows:

Width, in.	Thickness, in.
0.125	0.014–0.016
0.125	0.038
0.250	0.035
0.250	0.015
0.063	0.034

One of the obvious measures of geometry of this series is the original cross-sectional area. Figure 8 shows a plot of k vs. the initial area A_0. As A_0 increases from values near 10^{-2} to 5×10^{-2} sq cm the value of $k \times 10^3$ drops from about 6 to 1 min^{-1}. This demonstrates quite clearly that the parameter k

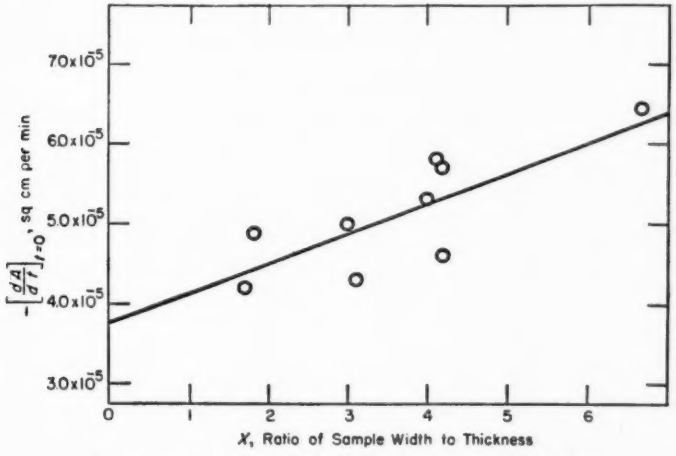

FIG. 10.—Plot of rate vs. width to thickness ratio, X. Natural rubber.

TABLE II

EFFECT OF λ_0 ON $\left[\frac{dA}{dt}\right]_{t=0}$ FOR NATURAL RUBBER

λ_0	F, kg per sq cm	$\lambda_0 F$, kg per sq cm	C, kg per sq cm	A_0, sq cm	$-k$ per min	$-\left[\frac{dA}{dt}\right]_{t=0}$ sq cm per min	ip, min
1.04	0.84	0.87	3.8	2.06×10^{-2}	4.0×10^{-3}	8.3×10^{-5}	135
1.06	0.84	0.89	2.5	2.06	3.3	6.9	170
1.09	1.3	1.4	2.6	2.10	2.8	5.9	70
1.09	1.3	1.4	2.5	2.10	3.0	6.2	70
1.18	2.3	2.7	2.5	2.12	2.0	4.2	~0
1.20	2.8	3.4	2.7	2.10	2.2	4.5	10
1.29	3.5	4.5	2.5	2.12	1.6	3.4	~0
1.30	3.3	4.3	2.3	2.12	1.5	3.2	0
1.38	4.1	5.7	2.4	2.12	1.3	2.8	0
1.50	5.0	7.5	2.3	2.14	1.2	2.5	0
1.62	5.2	8.4	2.1	2.14	0.8	1.8	0
1.73	5.8	10.0	2.1	2.16	0.8	1.7	0

Mix A cured 60 min at 140° C (ozone =32 pphm).

cannot give an absolute measure of rate of ozone attack, since it is so highly dependent on geometry. When the initial rate is calculated for the same series and plotted vs. A_0, Figure 9 is obtained. There is a dependence of rate on A_0, but it is much less pronounced than the dependence of k on A_0. A factor of 1.4 separates the extreme values instead of 6.0.

Another way to characterize the geometry of a specimen is to calculate the width to thickness ratio. This ratio is defined by X. The change in rate as X varies is similar to the behavior with A_0. Figure 10 is a plot of rate vs. X for a natural rubber gum vulcanizate. The slope and intercept of such plots for natural rubber and SBR are essentially equal.

This variation of rate with X (and A_0) leads to the problem of a standard value of X. One solution is to extrapolate to $X = 0$. This plan is prohibitive from an experimental view due to the amount of work involved. Another plan is to hold X constant and to refer to the rate as an "approximate" absolute rate. This procedure has been adopted for the work reported here. The value of X has been held at 7.5 ± 1.3. This variation of X results in a rate variation of

TABLE III

EFFECT OF λ_0 ON $\left[\frac{dA}{dt}\right]_{t=0}$ FOR SBR

λ_0	F, kg per sq cm	$\lambda_0 F$, kg per sq cm	C, kg per sq cm	$-k_1$ per min	A, sq cm	$-\left[\frac{dA}{dt}\right]_{t=0}$ sq cm per min	ip, min
1.03	1.4	1.4	[a]	20.5×10^{-3}	1.41×10^{-2}	5.0×10^{-5}	600
1.05	1.8	1.9	[a]	13.0	1.41	4.2	210
1.11	2.5	2.8	4.1	7.4	1.41	3.2	138
1.11	2.4	2.6	3.9	8.3	1.45	3.7	125
1.15	3.7	4.2	4.6	6.8	1.41	2.8	118
1.21	3.6	4.3	3.3	4.8	1.41	3.7	80
1.34	4.6	6.2	3.0	2.5	1.42	2.7	18
1.47	5.7	8.4	2.8	1.7	1.42	2.5	10
1.49	5.5	8.2	2.7	1.7	1.44	2.7	~0
1.60	6.2	9.9	2.6	1.4	1.45	2.4	0
1.73	7.0	12.2	2.5	1.0	1.45	2.0	0
1.84	7.2	13.3	2.3	0.8	1.41	1.8	0

Mix B cured 60 min at 150° C (ozone =37 pphm).
[a] Value of 4.0 used.

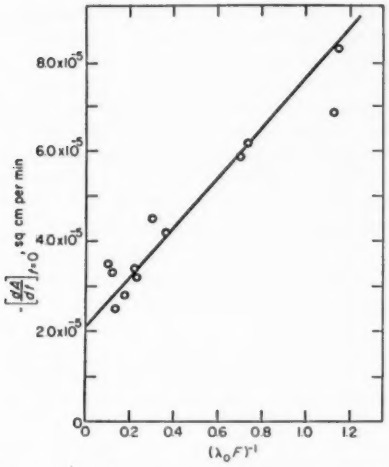

FIG. 11.—Plot of rate vs. $(\lambda_0 F)^{-1}$ for gum natural rubber.

±8 per cent at 40 pphm for a gum natural rubber. It is felt that this is a satisfactory procedure.

INITIAL ELONGATION

An examination of the effect of the initial extension ratio λ_0 on rate was carried out for natural and SBR gum rubbers. Initial extension ratios in the range of 1.03 to 2.12 were used. For each initial elongation, the value of C was determined and used for that specimen. The values for C decrease as λ_0 increases. This is in accord with the findings of previous workers and reflects the inability of Equation (1) to predict the exact elastic behavior of rubber.

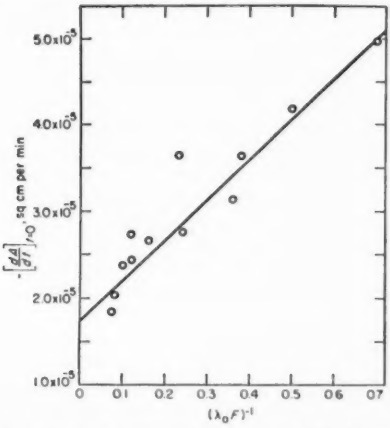

FIG. 12.—Plot of rate vs. $(\lambda_0 F)^{-1}$ for gum SBR rubber.

For the purposes of this report, the procedure as described is sufficient. The pertinent data for each elongation are listed in Tables II and III. In these tables F is the "modulus" or force per unit of unstrained area for the indicated initial extension ratio λ_0 and ip is the induction period. Both of these tables indicate that the rate and induction period decrease as λ_0 increases. By plotting rate vs. $(\lambda_0 F)^{-1}$ a linear relationship is obtained as shown in Figures 11 and 12. A similar relationship holds for the log of the induction period and $(\lambda_0 F)^{-1}$ as shown in Figure 13. The quantity $\lambda_0 F$ is a term encountered in the theory of the photoelastic behavior of vulcanized rubbers. It represents the force per unit actual cross-sectional area of a strained specimen. It is referred to as

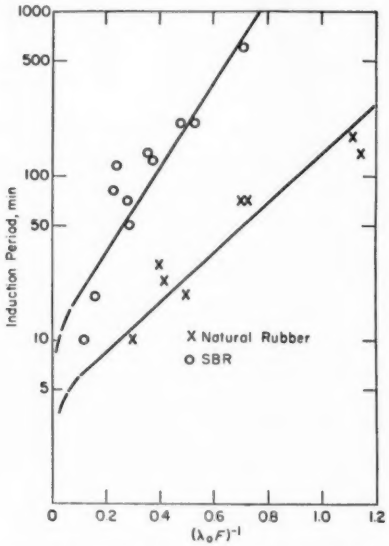

FIG. 13.—Plot of induction period, ip (on log scale) vs. $(\lambda_0 F)^{-1}$ for gum natural and SBR rubbers.

"stress" to distinguish it from the force per unit original cross-sectional area F or the modulus. The stress of an elongated specimen is related to the strain birefringence or degree of anisotropy by

$$\eta_1 - \eta_2 = \beta(\lambda_0 F) \tag{7}$$

where;

$\eta_1 - \eta_2$ = difference in principal refractive indexes or strain birefringence and
β = stress-optical coefficient.

This strain birefringence is due to a structural dissymmetry or anisotropic condition introduced into the originally isotropic rubber due to the presence of a strain. The relationship between rate and $(\lambda_0 F)^{-1}$ from a visually fitted re-

gression curve for natural rubber is

$$\left[\frac{dA}{dt}\right]_{t=0} \times 10^5 = 5.6(\lambda_0 F)^{-1} + 2.1 \tag{8}$$

for SBR

$$\left[\frac{dA}{dt}\right]_{t=0} \times 10^5 = 6.5(\lambda_0 F)^{-1} + 1.9 \tag{9}$$

Calculated correlation coefficients for these regression plots are 0.97 and 0.96, respectively, which indicate significant correlations. The fit to a linear relationship is reasonably good over the range of λ_0 studied. The intercept of these equations is the rate at infinite $\lambda_0 F$. Both values are nearly equal, and similarly the slopes are essentially equal.

It is of course necessary that strain be present for ozone cracking to occur. It is logical to expect that some dependence exists between strain and ozone cracking. Since strain serves to partially orient the polymer chains of a rubber, some relationship between this orientation and cracking should exist. An unelongated specimen is isotropic and imposing an elongation causes an anisotropic condition to exist. As previously indicated, the stress, or λF, is a direct measure of this. Should not the crack formation and growth behavior depend upon this parameter? At high values of $(\lambda_0 F)^{-1}$ the rate is high and induction periods are long. High values of $(\lambda_0 F)^{-1}$ represent a small degree of anisotropy. The rate is high for the reason that there are few cracks formed and their growth is unhindered. Many cracks at low $(\lambda_0 F)^{-1}$ values result in mutual interference and a low rate. Figure 14 is a plot of Newton's[5] showing the effect of elongation on initial crack density. At low elongations, no cracks are noted in the time intervals shown; that is the induction period has not been exceeded. At higher elongations the crack density increases. These are outdoor exposures so the ozone concentration is low.

At low initial elongations the number of cracks formed is small and growth occurs rapidly. How can growth occur rapidly if a high degree of anisotropy or orientation is needed? Actually a high degree of orientation is maintained at the locus of the growth, that is, the base or edge of a crack. The surface at the base is under a high strain (much higher than surface strain) in a protected region. The sides of the crack afford this protection and protect the growing region from interference by the development of adjacent cracks. This explains the dependence of rate on $(\lambda_0 F)^{-1}$.

The effect of $\lambda_0 F$ on the induction period is more straight forward. Long induction periods indicate that the probability of finding a number of polymer chains oriented in close proximity along the strain axis is small. When little orientation exists, the highly probable event of the formation of a crack requires a greater time to occur. The end of the induction period is most certainly preceded by the formation[5] of proto-cracks. These grow quickly, most probably by coalescence, into detectable cracks. This is signalled by creep of the specimen.

Ozone cracking can occur under two dissimilar conditions, either constant load or constant strain. The experimental technique for creep measurements strongly favors crack growth. This is due to the constant-load conditions. As cracks are formed and grow, they tend to open, growth being favored all the more by this. For constant strain conditions, an opposite tendency exists such

that crack growth is discouraged. This is caused primarily by a relaxation of stress. This relaxation in vulcanized gum rubbers although important, is not of great magnitude, but in filled rubbers, especially with carbon black, it is of greater magnitude. This poses the question—Which test condition should be employed? Technologically, in evaluating estimated service life from accelerated tests, the condition that most closely approximates service conditions should be chosen. In a theoretical sense when basic information is sought, the constant load test is to be preferred. It is to be preferred because λF can be computed and the relative degree of orientation is known.

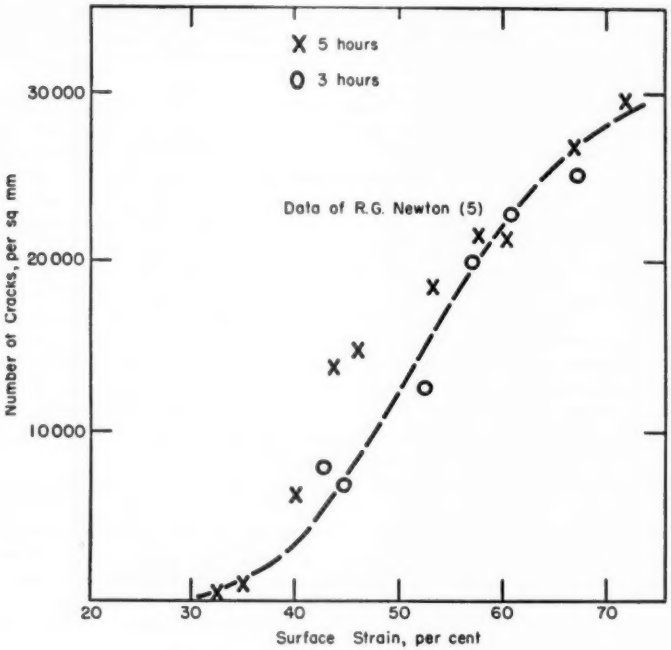

FIG. 14.—Plot of crack density vs. elongation.

Many references are found in the literature to the concept of critical strain in ozone cracking. Newton[5] discusses this in some detail and reports some of his own measurements on the phenomenon. The parameter to which strain is critical is usually crack size, although in many references the vague concept "degree of cracking" is used. It can be observed in Figures 11 and 12 that no maximum is in evidence in the rate vs. $(\lambda_0 F)^{-1}$ curves. A maximum in crack size means that there should be a maximum in rate of growth also. All reported accounts of a critical strain have involved a constant strain test specimen. The data presented here strongly argue against the existence of a critical strain. It is suggested that previous workers have been misled due to a combination of circumstances which complicate the situation, the two principal

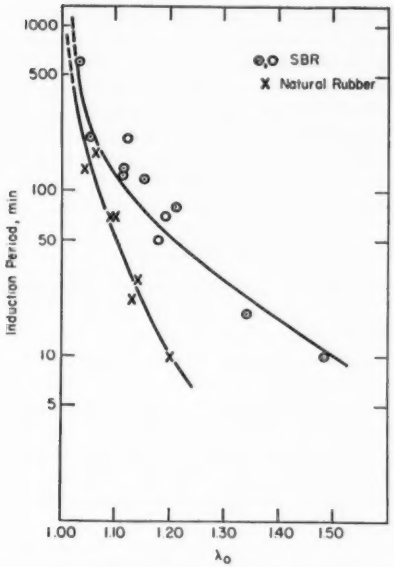

FIG. 15.—Plot of induction period, t_P (on log scale) vs. λ_0.

ones being stress relaxation and the existence of long induction periods prior to cracking. Figure 15 is a plot of induction period vs. λ_0 for gum natural and SBR rubbers. The very steep slope in the vicinity of 5 per cent elongation indicates that very long times indeed are to be expected at low elongations.

VARIATION OF RATE WITH TYPE OF RUBBER

A series of gum vulcanizates cured by conventional means was prepared using pale crepe, SBR 1502, nitrile rubber (Hycar 1042 and 1002), neoprene GN and W, and butyl 218. Creep measurements on this series were carried out at 90° F and at an ozone concentration of $81 \pm 3 \times 10^{-8}$ cu cm per cu cm or 81 ± 3 pphm. The initial extension λ_0 was selected so that approximately

TABLE IV

CREEP BEHAVIOR OF VARIOUS RUBBERS

Polymer	Induction Period, min	$-\left[\frac{dA}{dt}\right]_{t=0}$ sq cm per min
Pale crepe	<1	13.0×10^{-5}
SBR	20	13.0
Neoprene GN	1230	0.15
Neoprene W	1800	0.024
Butyl 218	5500	0.0038
Hycar 1002	30	4.5
Hycar 1042	35	4.3

Ozone = 81 ±3 pphm.
Temperature = 90° F.

equal values of $\lambda_0 F$ were obtained. Table IV gives the induction periods and initial rates for this series of rubbers. Both the induction period and the rate place the rubbers in the same relative order. This is an order that might be expected from experience. This arrangement of the various rubbers in regard to resistance to ozone cracking serves to add confidence in the technique. It also shows that in general a low rate is associated with a long induction period when the variable under study is the structure or chemical constitution of the polymer chain. The value of the creep technique lies in the fact that quantitative values are obtained in regard to resistance to ozone cracking.

SUMMARY

For reliable ozone testing a controlled ozone atmosphere is a necessity. There is a movement under way to correct the deficiencies of the ASTM Method D 1149-55T. These deficiencies are (*a*) the lack of a sufficient air throughput rate and circulation in the presently specified chamber and (*b*) difficulties encountered in the analysis of ozone. A new chamber and counter-current ozone absorption column that avoid the above-mentioned shortcomings are described.

As part of a program to obtain basic information on the phenomenon of ozone cracking, some preliminary results on the ozone-induced creep of gum vulcanizates are reported. The creep rate has been expressed in terms of the initial rate of cross-sectional area decrease due to ozone cracking. This rate is a measure of the collective growth of ozone cracks. Induction periods during which no creep occurs have been observed. The geometry of the test specimen is an important variable. An "absolute" rate of cross-sectional area decrease can be otained independent of specimen geometry. For practical reasons an approximate "absolute" rate is used where specimen geometry is maintained essentially constant.

The rate of cross-sectional area decrease is linearly related to the reciprocal degree of orientation of the network chains $(\lambda_0 F)^{-1}$. The logarithm of the induction period is also linear with $(\lambda_0 F)^{-1}$. Explanations for this particular dependence are offered. The rate of crack growth and the induction period for a series of common polymers were measured. Both parameters placed the polymers in the order that experience would indicate and lend confidence to the creep technique.

DISCUSSION

MR. A. F. SEREQUE.—What is the influence of the flow rate through the ozone chamber? Would doubling the flow rate be as severe as doubling the ozone concentration?

MR. A. G. VEITH (*author*).—In regard to our chamber the severity or rate of ozone attack in the 50 pphm range is not influenced by the flow rate at *constant* ozone concentration provided the flow rate is greater than 4 cu m per hr. If however the flow rate is reduced at constant *voltage* setting on the ozone lamp, then the concentration will change. This reduction of flow rate of course results in an increased concentration as measured by chemical analysis. Doubling the flow rate, again at constant voltage, will decrease the ozone concentration by approximately one-half. This would therefore have the opposite effect of doubling the ozone concentration providing sufficient internal circulation is present in both cases. In general an ozone chamber should always be operated at a flow rate-internal circulation condition such that the rate of cracking is independent of flow rate and internal circulation.

MR. SEREQUE.—Is the flow rate measured by standard flow meters or other devices?

MR. VEITH.—The flow rate is measured with a standard Fisher-Porter Flowrator calibrated in cu m per hr and operated at approximately room temperature and 14.7 psi atmospheric pressure.

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CHEMICAL ANTIOZONANTS AND FACTORS AFFECTING THEIR UTILITY *

WILLIAM L. COX

UNIVERSAL OIL PRODUCTS CO., DES PLAINES, ILL.

The advent of chemical antiozonants has granted to the rubber industry considerable relief from the problem of ozone-cracking which has plagued it to an ever-increasing extent throughout its history. This problem, enhanced in the past two decades by increased ozone in the atmosphere and by the widespread application of certain synthetic rubbers, can now be controlled if not eliminated by the judicious use of one of several materials specifically tailored to this purpose. However, unless the rubber manufacturer is conscious of the influence of a large number of variables upon the potential utility of a material as an antiozonant, to a large extent the usefulness of antiozonants may be lost to him.

The amount of antiozonant required to protect a rubber article from ozone degradation will depend upon such factors as:

1. Antiozonant structure,
2. Polymer type,
3. Other compounding ingredients, and
4. Exposure conditions.

It is hoped that this present survey will assist prospective antiozonant users in achieving more effective protection at decreased expense.

ANTIOZONANT STRUCTURE

In general it has been the experience of most workers in the field that the aromatic amines offer the greatest potentiality as rubber antiozonants. A comprehensive study of the effectiveness of arylene diamines as antiozonants has been reported by Shaw and others[9]. Selected data listed in this study have been shown in Table I to illustrate the effects of varying the number of aromatic rings, nitrogen and ring substituents, and the orientation of the amine groups. The results, generally, are in agreement with data from our own laboratories and may be summarized as follows:

1. An increase in the number of rings in the aromatic "nucleus" decreases the effectiveness.

2. Ring-substituted *p*-phenylenediamines are less potent than their unsubstituted analogs.

3. Compounds with aryl substituents on the nitrogen are considerably less effective than similar ones having alkyl substituents.

4. With respect to the arrangement of the amino groups on the ring, effectiveness follows the order

para > *ortho* > *meta*.

* Reprinted from "Symposium on Effect of Ozone on Rubber," ASTM Special Technical Publication No. 229, pages 57-71, September, 1958.

TABLE I

EFFECTIVENESS OF ARYLENE DIAMINES*

Antiozonant	Butadiene-styrene (BD-STY)	Parts per hundred parts of rubber, phr	ASTM Tentative Method D 1149-51T[b] Ozone chamber[c] Original 20 per cent elongation	Original BL	Outdoors 20 per cent elongation	Outdoors BL
N,N′-di-*sec*-butyl-*p*-phenylenediamine	90–10	2	12M	4M	>24M	24M
N,N′-di-*sec*-butyl-benzidine	90–10	2.7	12D	3M	6M	17M
N,N′-di-*sec*-butyl-1,4-naphthalenediamine	90–10	2.5	4H	2H	3D	3D
N,N′-di-*sec*-butyl-*p*-terphenylenediamine	90–10	3.4	2H	2H	3D	3D
N,N′-di-*sec*-butyl-*p*-phenylenediamine	90–10	2	12M	4M	>24M	24M
N,N′-di-*sec*-butyl-2-methoxy-*p*-phenylenediamine	90–10	2	7M	3M	1M	5M
N,N′-di *sec*-butyl-2-methyl-*p*-phenylenediamine	90–10	2	9M	4M	3M	6M
N,N′-di-*sec*-butyl-1,2,3,4-tetrahydro-5,8-naphthalenediamine	90–10	2.5 (+1 phr wax)	7H	5H	16M	7M
N,N′-bis(1-ethyl-3-methylpentyl)-*p*-phenylenediamine	80–20	3 (+1 phr wax)		>7M	>7M	>7M
N,N′-diphenyl-*p*-phenylenediamine		3 (+1 phr wax)		1D	>9W	>9W
N,N′-di-*β*-naphthyl-*p*-phenylenediamine		3 (+1 phr wax)		2H	2W	2W
N,N′-bis(1-isobutyl-3-methylbutyl)-*p*-phenylenediamine	80–20	3 (+1 phr wax)		>6W	>6W	>6W
N,N′-bis(1-isobutyl-3-methylbutyl)-*o*-phenylenediamine		3 (+1 phr wax)		2H	>2W	>2W
N,N′-bis(1-isobutyl-3-methylbutyl)-*m*-phenylenediamine		3 (+1 phr wax)		2H	7D	7D
N,N′-dioctyl-*p*-phenylenediamine	80–20	3 (+1 phr wax)		2H	>6W	>6W

[a] Data reported by Shaw, Ossefort, and Touhey[9].
[b] Tentative Method of Test for Accelerated Ozone Cracking of Vulcanized Rubber (D 1149-51T), 1955 Book of ASTM Standards, Part 6, p. 1162.
[c] H = hour, D = day, W = week, M = month, BL = bent loop.

5. Compounds with secondary alkyl substituents on the nitrogen are considerably more effective than those bearing primary alkyl groups.

Unfortunately, certain materials, such as N,N′-bis(*sec*-butyl)-*p*-phenylenediamine, while otherwise meeting the "qualifications" of a good antiozonant, suffer serious drawbacks in their toxicity and volatility. Furthermore, they may, when used in amounts needed for protection against ozone, serve as *pro-oxidants* in the reaction of the rubber with molecular oxygen. These factors of toxicity, volatility, and pro-oxidant character are avoided in the higher alkyl analogs without loss of antiozonant potency.

Ordinarily the common amine antioxidants and antiflex agents are much less potent than the arylene diamines as antiozonants, though heavy loadings of these materials in normally resistant polymers such as neoprene are reported to increase the ozone resistance markedly[11]. There is no reported data to show the same behavior on the part of the common phenolic antioxidants.

ANTIOZONANT PROTECTION AND EFFECT OF POLYMER TYPE

To protect a stock from ozone degradation, an additive must function in one or more of three possible ways:

1. Form a physical barrier over the rubber surface, thus preventing contact between ozone and rubber.
2. React preferentially with the ozone, thus leaving none to react with the unsaturation in the rubber molecules.
3. React with the rubber ozonide or a precursor in such a way as to prevent chain scission even though ozone reaches the double bond.

Waxes act in the first way only; antiozonants may react in all three ways—certainly in the first two.

Obviously then, any material added to prevent ozone-cracking must do so by reaching the surface of the rubber. This means that the amount of the additive required to give protection will depend to some extent upon its solubility and rate of diffusion in the given stock. Again, to react preferentially with the ozone in competition with the polymer double bonds, the amount of antiozonant required will be partially determined by the reactivity of the antiozonant toward ozone and by the reactivity and number (concentration) of the polymer double bonds at the surface. It is therefore not surprising that the amount of N,N′-diaryl-*p*-phenylenediamine required to protect a stock is greater than that of an N,N′-dialkyl-*p*-phenylenediamine, since, as can be shown from the data of Table II the reactivity of the diaryl compound toward ozone is considerably less than that of the dialkyl analogs. Nor is it surprising that the amount of an antiozonant such as UOP88 (Universal Oil Products Co.) required to protect a stock from ozone degradation under a given set of conditions (20 per cent elongation, 100°F, 50 parts per hundred million ozone (pphm O_3)) increases from neoprene (<1 part per hundred parts of rubber (phr)) to SBR (2 to 3 phr) to Hevea stocks (4 phr), since the reactivities of the double bonds increase in the same manner. Similarly, data of Lundberg et al.[6] indicate that the amount of UOP88 required to protect butyl stocks from ozone increases with the increase in unsaturation of the butyl polymer.

One must, however, always bear in mind that all the effects of antiozonant solubility, diffusion rate, and reactivity, and of double bond numbers and reactivity are superimposed, and that the resultant picture may seem at odds with conclusions drawn from individual considerations. This is amply illus-

TABLE II

RELATIVE RATE FACTORS [a]
Reaction of ozone with antiozonant vs. SBR unsaturation

Antiozonant	k_a/k_r [b]
N,N′-di-*sec*-butyl-*p*-phenylenediamine	320
N,N′-bis(1-methylheptyl)-*p*-phenylenediamine	275 to 340
N,N′-bis(1-ethyl-3-methylpentyl)-*p*-phenylenediamine	250
p-phenylenediamine	200
N-phenyl-*p*-phenylenediamine	120
N,N′-diphenyl-*p*-phenylenediamine	25
N,N′-di-β-naphthyl-*p*-phenylenediamine	32
Benzidine	4
p-methylenedianiline	—[c]

[a] Calculated from data of Delman et al.[4].
[b] k_a = specific rate constant − ozone + antiozonant.
k_r = specific rate constant − ozone + olefinic bond.
[c] Faster viscosity decrease than for control.

trated by the increasing response to amine antiozonants of SBR polymers as the styrene-butadiene ratio is decreased, even though the double bond concentration increases[9]. Apparently, this latter factor is outweighed by diminished antiozonant solubility or an increased rate of diffusion with increasing butadiene content, or both.

COMPOUNDING INGREDIENTS

Even though a definite polymer-antiozonant combination is to be used under a given set of exposure conditions, there is still a wide range of antiozonant requirements possible, depending upon the compounding ingredients chosen. Because of the highly reactive nature essential to the antiozonant, the surface characteristics of the reinforcing agent, and the type and reactivity of the vulcanization intermediates, it is possible to lose during the curing process a large

TABLE III

CARBON BLACK TYPE AND ANTIOZONANT EFFECTIVENESS

Carbon black	Approximate areas, sq m per g	pH	Per cent oxygen in black[a]	Per cent UOP88 extractable from vulcanizate[b]	Hours to first crack of vulcanizate[b] 100 F—50 pphm ozone — Elongations		
					25 per cent	20 per cent	15 per cent
None	—	—	—	97.1	>336	>336	>336
MT[c]	7	7.4	—	92.2	>336	>336	>336
FT[c]	18	7.2	—	91.6	>336	>336	>336
SRF[d]	20	9.4	0.37	89.9	>336	>336	>336
HAF[d]	70	9.2	0.71	88.6	>336	>336	>336
FEF[d]	40	9.3	0.97	87.9	>336	>336	>336
ISAF[d]	100	9.1	—	80.6	>336	>336	>336
SAF[d]	~140	—	2.21	74.5	>336	>336	>336
HPC[d]	~160	4.0	3.25	64.8	3	6	16
EPC[d]	110	4.3	3.71	61.9	2	2	6

[a] Data of Studebaker and coworkers[10] with corresponding Cabot & Phillips blacks.
[b] 50 phr black in SBR 1502; 3 phr UOP88.
[c] Thermatomic.
[d] United carbon.

percentage of the antiozonant originally added, unless care is taken in the selection of the other materials in the compound. The influence of common compounding ingredients upon the per cent of UOP88 extractable, after vulcanization, is discussed in the next sections. It has been our experience at the Universal Oil Products Co. that the ozone resistance of similar stocks parallels the extractable antiozonant.

Carbon black.—It has been reported in the literature that "carbon black, regardless of type, particle size, structure, and physical properties does not affect the rate or degree of checking or cracking in natural rubber or low-temperature polymer compounds when subjected to weather or ozone exposure"[7]. This seems to be the case for antiozonant-free stocks (though *any* improperly dispersed pigment may increase the ozone susceptibility of a compound by setting up "abnormal" stresses around the pigment particles). However, the carbon used *will* play a large part in determining the effectiveness of a given amount of antiozonant in a compound. As shown in Table III, the amount of

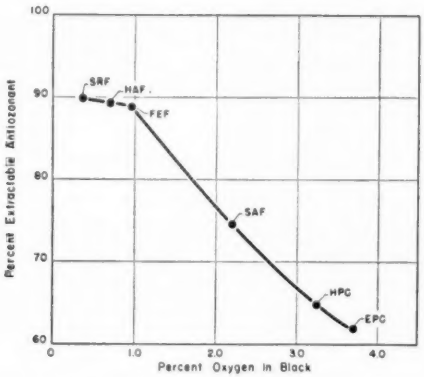


FIG. 1.—Correlation of extractable antiozonant with oxygen content of carbon blacks.

UOP88 remaining extractable from an SBR stock after vulcanization may vary from 60 to 100 per cent of that originally added, depending solely upon the amount and type of black used. In general, the thermal and furnace blacks show good retention, the channel black poor retention of antiozonant. The amount of antiozonant remaining extractable correlates with such factors as pH and surface area only to a limited extent. It does, however, correlate well with the oxygen content of the black, as shown by comparison in Table III and in Figure 1 with oxygen values reported by Studebaker and coworkers[10] for similar blacks.

That this loss in extractable antiozonant affects the ozone resistance of the stock is verified by the data in the tables and by the top two specimens of Figure 2. These latter differ only in the type of black, yet the EPC (easy processing channel) black stock is badly cracked, while the HAF (high abrasion furnace) black stock is crack-free.

Additional verification is pictured in Figure 3, which shows the results of dynamic ozone tests on the specimens described in Table III above. The samples are arranged from top to bottom in order of increasing extractable-

antiozonant content. The agreement of the ozone resistance with the amount of extractable antiozonant is marked.

Curing-system.—For a given carbon black-polymer system, the protection afforded by an antiozonant such as UOP88 will vary markedly with the type of curing system used. It has been found that thiazole-accelerated sulfur vulcanizates containing antiozonant are far more ozone-resistant than similar so-called sulfurless vulcanizates prepared from thiuram disulfides, or those using diphenylguanidine (DPG) acceleration. (Rock Island Arsenal data indicate excellent ozone resistance for an SBR vulcanizate containing UOP88

(*a*) Carbon black—EPC (easy processing channel),
Curing system—2 phr sulfur, 2 phr benzothiazolyl disulfide,
Hours to first crack—31 to 47.

(*b*) Carbon black—HAF (high abrasion furnace),
Curing system—2 phr sulfur, 2 phr benzothiazolyl disulfide,
No cracks in 239 hr.

(*c*) Carbon black—HAF (high abrasion furnace),
Curing system—4 phr tetramethylthiuram disulfide;
Hours to first crack—7 to 23.

(*d*) Carbon black—HAF (high abrasion furnace),
Curing system—2 phr sulfur, 1 phr Santocure,
No cracks in 239 hr.

FIG. 2.—SBR specimens exposed to ozone at 100° ±2° F, 20 per cent elongation, 52 hr at 33 ±5 pphm ozone, then 187 hr at 63 ±5 pphm ozone.

when a Tetrone A-Captax system is used.) This is partially illustrated by Figure 2 where benzothiazolyl disulfide (MBTS) and Santocure-accelerated sulfur vulcanizates are compared after equal ozone exposures with analogous tetramethylthiuram disulfide (TMTD) vulcanizate.

As was the case with the carbon blacks there again is a correlation between the amount of antiozonant extractable after vulcanization and the ozone resistance of the stock. Indeed, within any one type curing system, the amounts of accelerator and sulfur affect the extractable antiozonant values and thus may be expected to affect the ozone resistance of the resulting compound.

The effects of accelerator type and concentration and of sulfur concentration are shown in Table IV. It will be noted that an *increase* in accelerator or sulfur concentration results in *decreased* antiozonant extractability.

Antiozonant-wax combinations.—The incorporation of wax into an antiozonant-containing stock generally serves to reduce the amount of antiozonant required for crack-free static performance. At the same time, the wax will at best have no beneficial effect on the dynamic ozone-resistance and usually will decrease it. The most obvious explanation is that the wax, in a static test, by

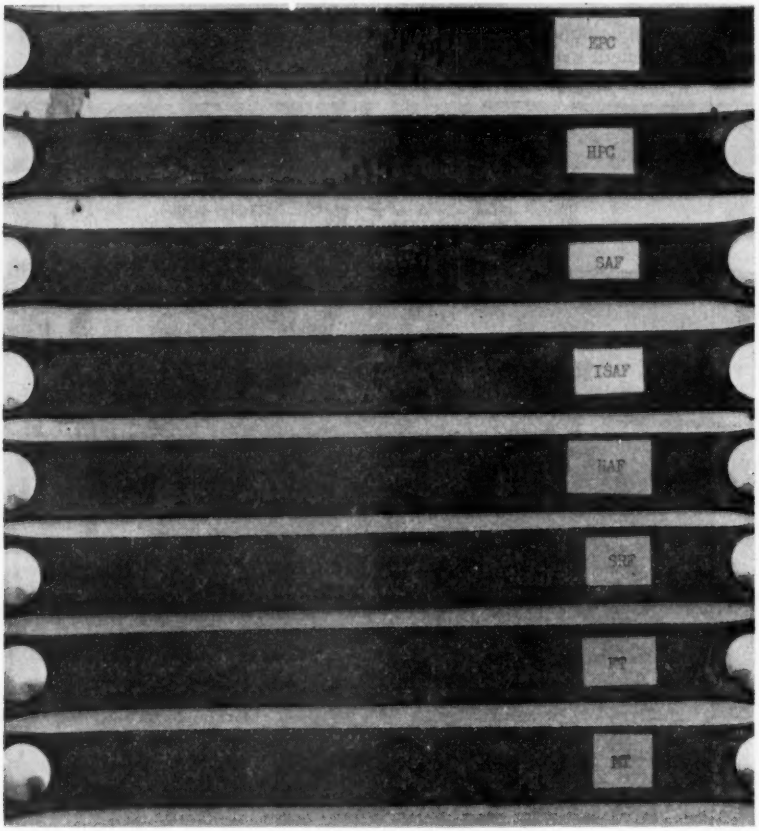


FIG. 3.—Dynamic ozone tests. Bent loops—320 flexes per min; 60 pphm ozone; room temperature; 24 hr. All stocks contain 50 phr carbon black and 3.0 phr UOP88 (United Carbon carbon black).

forming its physical barrier decreases the effective ozone concentration at the rubber surface, thus decreasing the amount of antiozonant required to prevent the ozone degradation. In dynamic tests, however, the wax film is being continually ruptured and may pull antiozonant away from the rubber surface as the breaks in the wax film occur.

One should always be aware, however, of the possibility of losing some of the *static* ozone resistance of a wax-loaded stock when adding *certain* antiozonants.

TABLE IV

EFFECT OF CURING SYSTEM ON ANTIOZONANT RETENTION IN SBR STOCKS AFTER VULCANIZATION
All contain 3.0 phr UOP88; 40 phr HAF black

Compound	Accelerator	Sulfur, phr	Extractable antiozonant, per cent
1082	2.0 phr MBTS	2.0	66.4
1083	1.0 phr MBTS	2.0	79.6
1087	None	2.0	~100
1088	1.0 phr MBTS	3.0	74.6
1083	1.0 phr MBTS	2.0	79.6
1089	1.0 phr MBTS	1.0	88.6
1083	1.0 phr MBTS	2.0	79.6
1084	1.0 phr Santocure	2.0	81.6
1093	1.0 phr DPG	2.0	~18.0
1085	2.0 phr TMTD	—	35.0
1090	4.0 phr TMTD	—	12.9

We have noted in our laboratory that certain experimental antiozonants when added to a natural rubber vulcanizate containing a paraffin wax *decrease* the static ozone resistance, though in the same stock other added antiozonants have definite beneficial effects. Quite probably this detrimental effect of the former is similar to the behavior of certain softeners and asphaltic hydrocarbons reported by Cutting[3].

TEST CONDITIONS

As a general statement one can say that any factor, such as geometry of specimen, strain, ozone concentration, temperature, etc., which affects the susceptibility of the antiozonant-free stock to ozone degradation, will have a qualitatively similar effect on the analogous stock containing antiozonant. In other words, anything which enhances the vulnerability of the rubber compound to ozone will increase the amount of antiozonant required to protect the stock. We shall consider possible reasons for this below.

Specimen geometry.—One of the most important factors in determining the amount of antiozonant required to protect a compound from ozone cracking under a given set of exposure conditions is the shape of the test specimen. The reason for this statement is clear from Figure 4. Here is one cross-section are included the typical specimen shapes—flat, rounded, square, and angled (both acute and obtuse). Around the specimen has been drawn a band to illustrate

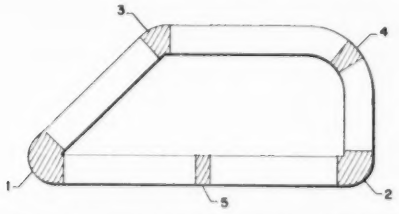


FIG. 4.—Ozone resistance and specimen geometry. Numbers indicate order of vulnerability to ozone attack.

the "reactive-ozone" region. The shaded areas indicate the portion of the zone within perpendicular reaction distance of equal lengths of rubber surface around the various angles and curves. It is easily seen that the order of susceptibility to ozone attack should follow the size of the various areas. That this is the case we have found repeatedly with a wide variety of stocks. The edge effects exhibited in specimens of rectangular cross-section are quite marked. Specimens containing increasing amounts of antiozonants almost inevitably proceed from general cracking (both edge and surface) at very low concentration, to edge cracks only at greater concentration, and finally no cracks whatsoever. Consequently there is quite often a significant difference in the antiozonant requirements of a flat-surfaced specimen and of one containing sharp edges. This is illustrated in Table V where the antiozonant requirements of an

TABLE V

EDGE EFFECTS AND ANTIOZONANT REQUIREMENTS
50 pphm O_3; 100°F; 2 weeks

Antiozonant	Elongation, per cent	Antiozonant requirement, phr[a]	
		Edge	Surface
A	10	2.25	1.75
	20	2.5	2.25
B	10	2.75	1.75
	20	>3.0	1.75
C	10	>3.0	2.75
	20	>3.0	>3.0
D	10	>3.0	1.50
	20	>3.0	2.25
E	10	1.75	1.50
	20	2.75	2.25

[a] ± 0.25 phr.

SBR sidewall stock are compared on the basis of edge cracking or surface cracking. Neglecting edge effects, it is seen that compound D appears at least equal in effectiveness to any other, yet if edge effects are considered, the same material appears to be one of the worst.

Specimen conditioning.—Most investigators have followed the ASTM Method D 1149-51T (Tentative Method of Test for Accelerated Ozone Cracking of Vulcanized Rubber (D 1149-51T), 1955 Book of ASTM Standards, Part 6, p. 1162) procedure of allowing the stressed specimen to remain 24 hr in a closed cabinet at room temperature before exposure to ozone. No recommendation has been made, however, as to the age of a specimen before exposure, though in certain studies of protective waxes, the age of the specimen has been shown to have a direct effect on measured ozone resistance[8].

In the case of antiozonant-containing stocks, age appears to be of less importance. Perhaps this is due to the more rapid rates of diffusion of antiozonants. Occasionally, however, an effect of age is noted, as illustrated in Figure 5 for a natural rubber tread stock. Here a specimen stored for one month before ozone exposure was considerably more ozone-resistant than a specimen of the same stock exposed one week after vulcanization. Indications are that the antiozonant continually diffuses to the surface during storage, so that the older specimen should have had a considerably higher initial surface concentra-

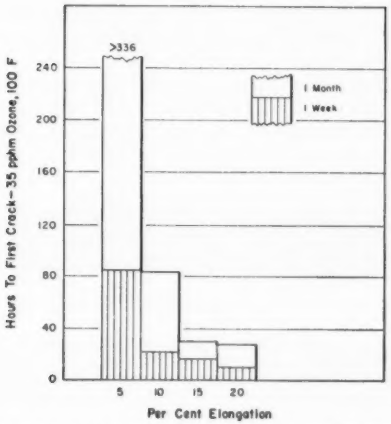


FIG. 5.—Ozone resistance of natural rubber tread stock containing antiozonant as a function of specimen age, 35 pphm ozone, 100°F.

tion of antiozonant. Upon ozonization, the antiozonant used in this stock develops a definite physical barrier from the ozonized products. Therefore, upon exposure the older specimen would achieve a greater extent of protection through physical barrier formation than would the newer one, and thus appear more ozone-resistant.

In specimens stored for a year or more before exposure, another factor—direct oxidation of the antiozonant within the sample by molecular oxygen—

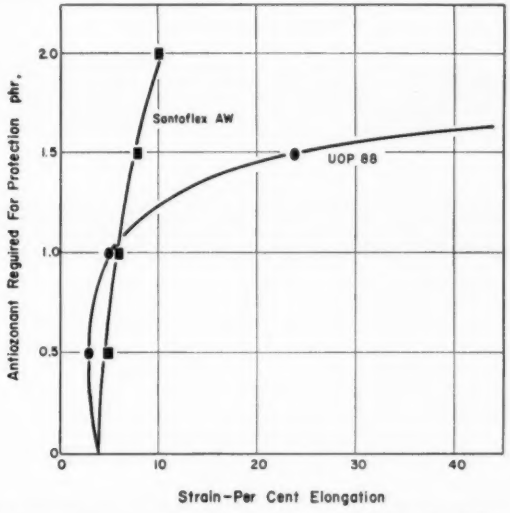
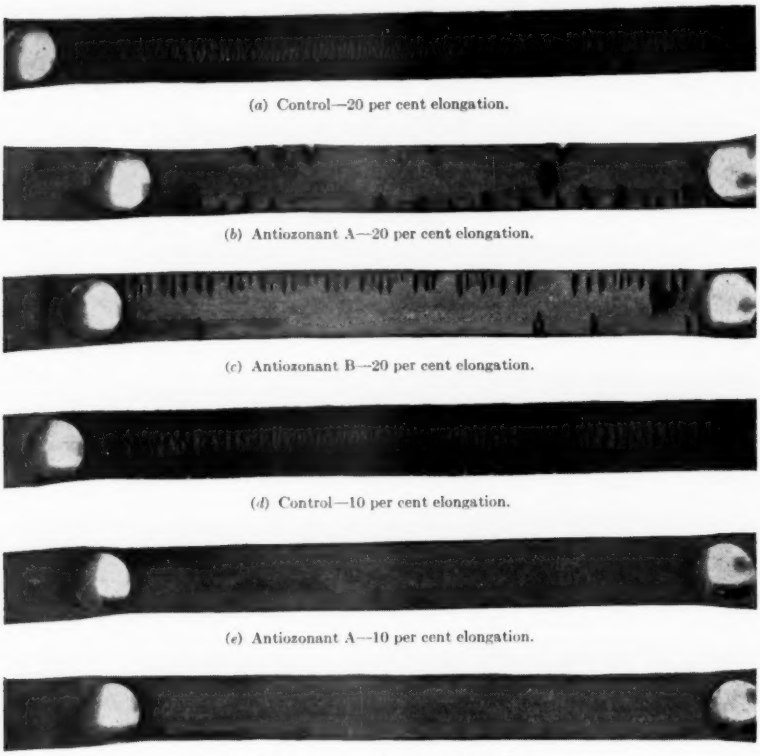


FIG. 6.—Antiozonant requirement vs. strain. Data of Edwards and Storey[4], 25 pphm ozone, 100°F.

enters the picture. This is reflected in decreased antiozonant extractability and decreased ozone resistance similar to that which occurs on oven-aging of specimens before exposure[9].

Strain.—It has long been known that before a rubber specimen will crack in the presence of ozone it must be under a certain amount of strain. Within limits, the more the strain applied to the sample exceeds this "threshold" value, the faster will the stock crack[12]. It is not surprising then to see the antiozonant



(*a*) Control—20 per cent elongation.

(*b*) Antiozonant A—20 per cent elongation.

(*c*) Antiozonant B—20 per cent elongation.

(*d*) Control—10 per cent elongation.

(*e*) Antiozonant A—10 per cent elongation.

(*f*) Antiozonant B—10 per cent elongation.

FIG. 7.—Specimens exposed to 30±5 pphm ozone at 100°F for 2 weeks.

requirements of a stock increase with increased strain. That this is the case has been shown previously by Edwards and Storey[5], whose data are plotted in Figure 6. The importance of elongation in antiozonant testing is still further pointed out in Figure 7 which shows specimens of a base stock with and without added antiozonants exposed simultaneously to ozone at two different elongations. For both antiozonant-containing specimens, the 10 per cent-elongated specimens are crack-free, but the 20 per cent-elongated specimens show both edge and surface cracks.

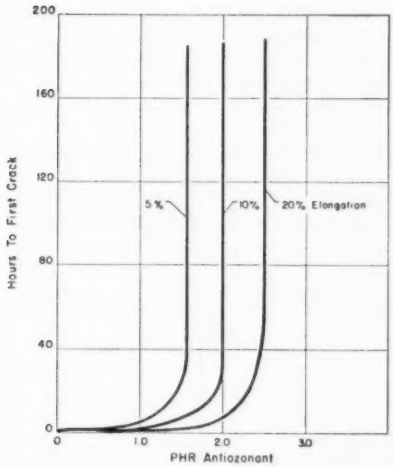


FIG. 8.—Effect of elongation upon the ozone resistance of an SBR sidewall compound containing varying amounts of antiozonant, 50 pphm ozone, 100°F.

Similar data have been obtained in our laboratories with all antiozonants tested. A typical example of the effect of elongation upon the cracking characteristics of a set of stocks containing varying amounts of a given antiozonant is shown in Figure 8. In all cases, increased strain raises the level of antiozonant required to give crack-free performance and decreases the time required for cracks to appear in stocks containing insufficient antiozonant.

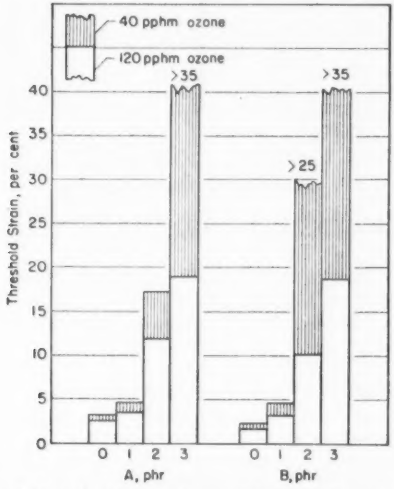


FIG. 9.—Threshold strain of SBR stocks containing two different antiozonants—sharp-edged specimens.

As noted above, for all antiozonants tested, the *qualitative* effect of increased strain is the same. The *quantitative* effects may differ greatly however. Some materials which afford low antiozonant requirements at low elongations (~5 per cent) may seem almost ineffective at higher ones (20 per cent), while others show only a comparatively mild effect of strain on antiozonant requirement (Figure 6).

Ozone concentration.—As might be expected, an increase in the ozone concentration results in an increased rate of reaction of ozone with polymer and antiozonant. This results in faster cracking and lowering of the threshold strain values for antiozonant-containing stocks. This is shown in Figure 9 for

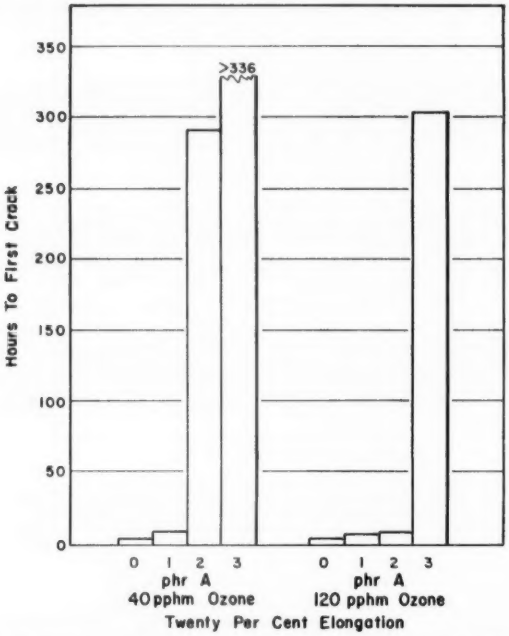


FIG. 10.—Effect of ozone concentration on the ozone resistance of SBR stocks containing antiozonant A—sharp-edged specimens.

stocks containing various concentrations of two different antiozonants in ozone concentrations of 40 and 120 pphm. Similarly, the amount of antiozonant required to give crack-free performance at fixed strain and temperature conditions increases with increased ozone concentration. This is demonstrated for these two materials in Figures 10 and 11.

As mentioned previously, the antiozonant may be considered to be an ozone scavenger. It competes with the rubber for the available ozone molecules. When there is sufficient antiozonant at the surface to eliminate the ozone-polymer reaction, cracking is prevented. If one considers a simplified mechanism for antiozonant action, assuming that there is a certain definite surface antiozonant concentration, c_{As}, (under fixed temperature and strain conditions)

above which the rubber will be crack-free but below which cracking will occur, then the relationship of the threshold antiozonant concentration, c_A, required within the stock to maintain this surface concentration, to the ozone concentration in the atmosphere, c_{O3}, may be shown to be

$$c_A = c_{A_0} + \frac{K_O}{nK_A} c_{O3}$$

where K_O and K_A are the respective diffusion constants for the ozone to the surface and for the antiozonant through the polymer to the surface (n repre-

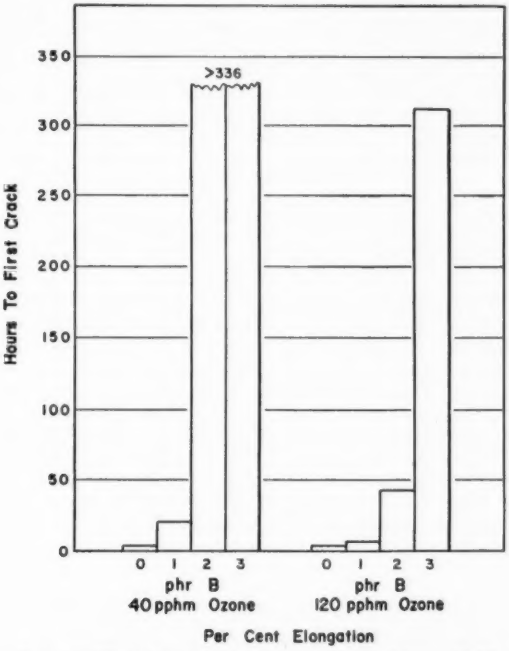


FIG. 11.—Effect of ozone concentration on ozone resistance of SBR stocks containing antiozonant B—sharp-edged specimens.

sents the number of ozone molecules reacting per molecule of antiozonant). This then is in agreement with the results reported above. One should note that the quantitative effect on antiozonant requirement of changing ozone concentration should depend among other things upon the rates of diffusions of both ozone and antiozonant. This means that the relative merits of materials judged at extremely high ozone concentrations may not reflect their true relationships in low ozone atmospheres.

Temperature.—While several studies of the effect of temperature upon the ozone-resistance of unprotected stocks or of wax-containing stocks have been published[1,2], only the paper of Lundberg and his associates[6] includes data on the effect of temperature upon the cracking of antiozonant-protected com-

pounds. Here there appears to be little difference between 100°F and 110°F as to survival of the material in a crack-free state in 25 pphm ozone. Verbal reports, however, from various sources indicate the need of higher antiozonant loadings at higher temperatures.

If we once again consider the simplified ozone-scavenger mechanism, so that

$$c_A = c_{A_s} + \frac{K_O}{nK_A} c_{O_3} \text{ (atmos)}$$

we see that the increased polymer reactivity toward ozone accompanying increased temperature should require a greater surface concentration of antiozonant to prevent such reaction, thus increasing the antiozonant concentration required in the stock. However, the over-all effect will also be determined to a great extent by the relative changes in diffusion rates of ozone and antiozonant, which may act so as to negate or to enhance the effect of increased polymer reactivity. Quite obviously, whichever happens will depend ultimately on the antiozonant used.

CONCLUSIONS

To obtain the maximum effectiveness from antiozonants such as the N,N′-dioctyl-*p*-phenylenediamines in any given stock, information to date indicates the desirability of:

(*a*) The selection of proper antiozonant-polymer combination.

(*b*) The use of low-oxygen-content reinforcing blacks (thermal or furnace rather than channel).

(*c*) The use of a thiazole-accelerated sulfur cure.

(*d*) The proper design of product to avoid cured-in strain and sharp edges.

The choice of antiozonant concentration will depend in part on strain, ozone concentration, and temperature to be encountered in service, as well as the type of service—static or dynamic—and the desired crack-free life of the article. Only through a consideration of all these factors can the maximum results from chemical antiozonants be achieved.

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PREVENTION OF OZONE ATTACK ON RUBBER BY USE OF WAXES *

S. W. Ferris, S. S. Kurtz, Jr., and J. S. Sweely

Sun Oil Co., Marcus Hook, Pa.

The tendency for stretched rubber, when subjected to outdoor exposure, to form cracks perpendicular to the direction of stress was originally known as sun-cracking. The work of Newton[10] showed that light was not necessary and identified ozone as the causative agent. That ozone is the principal factor there seems to be no doubt, but we cannot assert that it is the sole factor. Some test specimens, for example, have been found to crack in the shade, but not in the sun, and some investigators suspect that certain atmospheric pollutants may have a modifying effect.

It has been known since 1881[8] that addition of wax to the rubber compound will provide protection against this type cracking. Garvey and Emmett[6] found that oils or oil-like materials would also effect improvement, but by far the major portion of work has been done with petroleum waxes.

The two broad classes of petroleum waxes are paraffin and microcrystalline. The value of the literature—and this applies to many fields other than ozone cracking—is sharply limited by the tendency to characterize waxes as either paraffin wax or microcrystalline wax. As a matter of fact, the composition of petroleum waxes is complex, so that there are large differences in composition between different paraffin waxes and different microcrystalline waxes, with resultant differences in their performance when added to rubber.

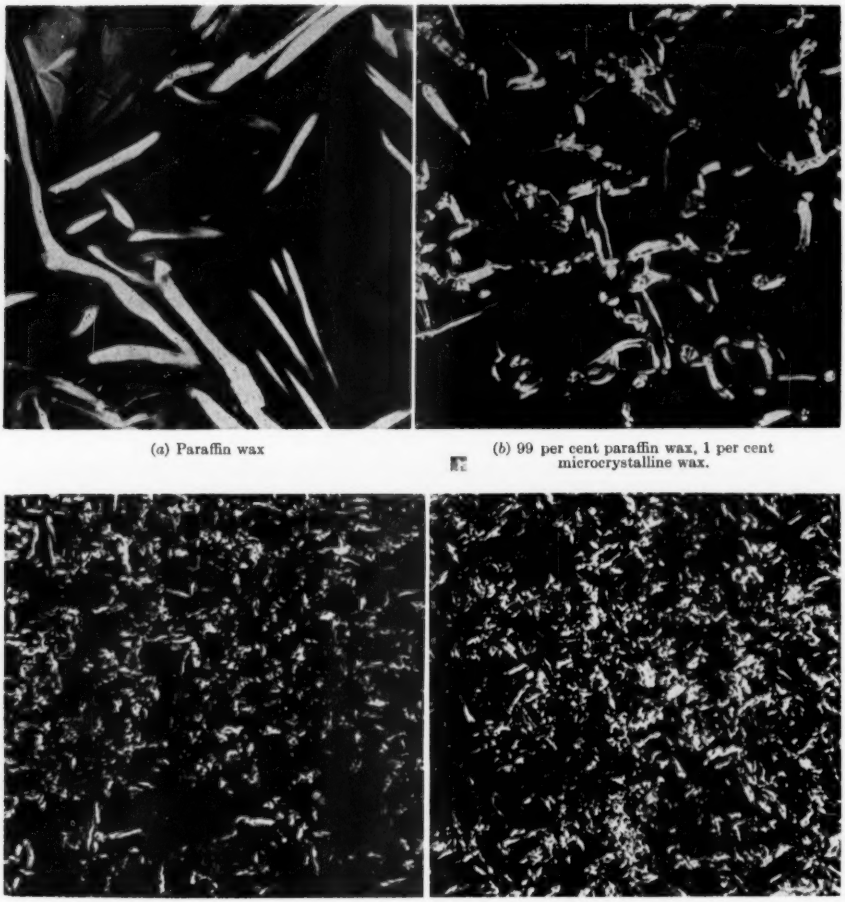
THE MECHANISM OF PROTECTION

It is agreed that wax makes its way to the surface of the rubber (blooms) and forms a film which protects by keeping the ozone from contact with the rubber.

Best and Moakes[2] studied vulcanized pure-gum rubber prepared from wax-containing compounds. With small additions of either paraffin or microcrystalline wax, no wax crystals could be observed in the vulcanizate, but a concentration was reached—presumably indicating the solubility of wax in rubber—above which crystals were found. Furthermore, they found no migration of wax to the surface unless crystals were visible in the rubber. The surface film was also found to be crystalline, with the crystals of much the same character as those within the rubber. The thickness of the bloomed films varied with temperature, type of wax, and time after cure, from less than 1 μ to about 14 μ.

The work of Best and Moakes seems to confirm that no protective film of wax will be formed until enough wax has been added to the rubber formula to exceed the solubility of the wax at whatever temperature it is desired to confer protection. Blooming (crystallization) of wax on the surface of rubber is probably about the same as the blooming of free sulfur—just a solubility effect.

* Reprinted from "Symposium on Effect of Ozone on Rubber", Special Technical Publication No. 229, American Society for Testing Materials, 1958, pages 72–87.



(*a*) Paraffin wax

(*b*) 99 per cent paraffin wax, 1 per cent microcrystalline wax.

(*c*) 95 per cent paraffin wax, 5 per cent microcrystalline wax.

(*d*) Microcrystalline wax.

FIG. 1.—Comparison of crystal structure of paraffin and microcrystalline wax in transmitted polarized light.

Wax originally crystallized in the rubber may possibly redissolve and migrate to the surface to escape a slight internal pressure in the rubber.

Not all waxes which bloom to the surface will provide adequate protection, and the differences between various wax layers presumably involve two factors: the tenacity with which the crystals adhere to the rubber surface, and the type of crystals. The more desirable type of crystal would pack closely, preferably layer upon layer, in order to provide an effective barrier to the passage of ozone.

Compared to microcrystalline wax, paraffin is of lower molecular weight and viscosity, usually contains a higher proportion of normal paraffin hydro-

carbons, and is obtained from a distillate petroleum fraction, whereas microcrystalline wax is derived from a residual fraction.

Crystals of paraffin wax tend to be large and of fairly regular outline. Microcrystalline waxes give much smaller crystals, frequently of irregular outline. When, however, microcrystalline wax is added to paraffin wax, the microcrystalline wax impresses its form on the paraffin. This is illustrated by the four photomicrographs, shown in Figure 1. These photographs were taken at 100 magnification, which is adequate for this type of study. Even 1 per cent of the microcrystalline wax profoundly alters the crystals of the parafin. With 5 per cent of microcrystalline wax, the characteristics of the paraffin wax are almost completely lost.

It is well known that antichecking waxes are frequently mixtures of paraffin and microcrystalline waxes, but it will be apparent from Figure 1 that microscopic examination of the crystals of such blends will not reveal the presence of paraffin wax unless microcrystalline wax is almost completely absent.

METHODS OF TESTING

There have been many variations in the exposure testing of rubber in ozone cabinets[1,3–6,10] including variations of ozone concentrations and many attempts to correlate cabinet results with outdoor exposure tests. Sharpe[11] found that ". . . accelerated methods, although useful, give questionable results in testing of rubber in which waxes are used", and that ". . . erroneous conclusions . . . may be drawn . . . as compared with an outdoor exposure test. . . ." But results of outdoor exposures also vary with the location. Lundberg, Vacca, and Biggs[9] found this not surprising—in view of different ozone concentrations, different intensities of ultraviolet radiation, different temperatures, and variations in rain, frost, snow, and surface dirt conditions. Nevertheless, they found good correlation between ozone chambers and outdoor exposures on neoprenes, natural rubbers, nitrile rubbers, and 2½ and 3 per cent unsaturated butyl compounds. Poorer correlation was found with 1 and 2 per cent unsaturated butyl compounds.

Los Angeles exposure is generally considered severe because of the high ozone concentrations. Lundberg et al.[9] found that for specimens initially exposed in the summer of 1954, Los Angeles, Calif. and Yuma, Ariz., gave more checking than Murray Hill, N. J. When, however, tests were started in November, Los Angeles and Murray Hill gave about the same percentage of failures.

While reasonable reproducibility of exposure conditions can only be achieved in ozone chambers, rubber articles must perform satisfactorily under the exposure conditions normally encountered, whether or not they pass a given chamber test. It appears, therefore, that screening tests should be carried out in ozone chambers, but that the results should be verified by long-time exposure tests, choosing the location, or locations, and time of first exposure to approximate service conditions reasonably well.

It has been our experience that temperature of initial outdoor exposure plays a very important part. For instance, specimens exposed outdoors in the summer may behave quite differently from similar specimens placed on test in the winter. Both the incidence and extent of cracking can be affected. This is not surprising when one considers that during cold weather: (1) the migration rate of the waxes is slowed down; (2) the wax film may be considerably more brittle than under warmer conditions; (3) different stress effects exist in the rubber; and (4) the rate of reaction of ozone with rubber is lowered.

In an effort to simulate these temperature effects more closely, waxes are evaluated in some laboratories at both high and low temperatures.

The ozone tests reported in this paper were carried out as follows: For elevated temperatures up to 120° F, a commercially available ozonator, manufactured by G. F. Bush Associates, Princeton, N. J., was used. Generally, ozone concentrations of 25 parts per hundred million (pphm) and a temperature of 120° F were employed, although concentrations up to 100 pphm were used in some tests.

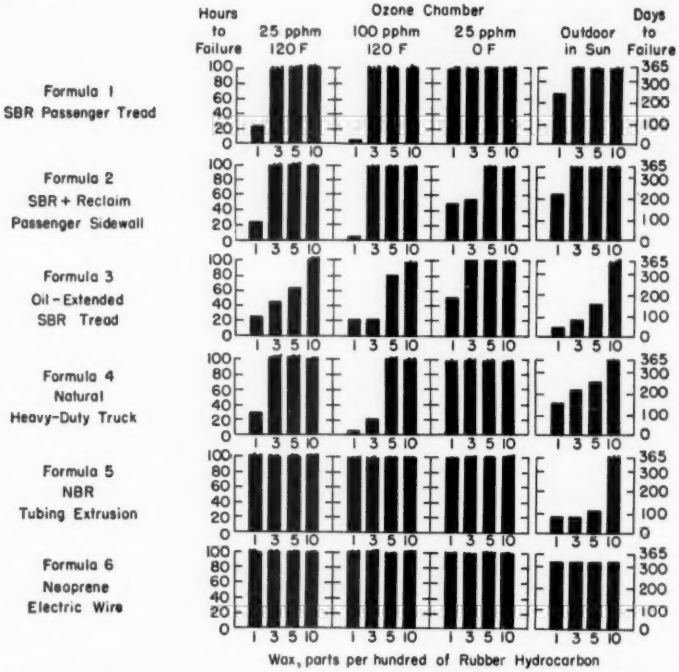


FIG. 2.—Comparison of exposure results under various conditions for various types of rubber. Jagged lines at the tops of bars indicate that the specimen showed no failure at the end of the test.

At temperatures down to 0° F, the authors tested in a chamber of their own design which incorporated some of the features of the Bush ozonator. These tests are run at an ozone concentration of 25 pphm. The procedures used for the ozone tests followed Tentative Method of Test for Accelerated Ozone Cracking of Vulcanized Rubber (D 1149-55T), 1955 Book of ASTM Standards, Part 6, p. 1162.

Outdoor exposure tests were run on the roof of the laboratories with the sample facing south at an angle of 45 deg. In most of the work the specimens were exposed for one year, so that they went through both a summer and winter season. Test strips for both the accelerated and the outdoor exposure tests were either in accordance with Method of Test for Resistance to Surface Cracking of Stretched Rubber Compounds (D 518-44), 1955 Book of ASTM Standards, Part 6, p. 1157, or Tentative Method of Test for Weather Resistance

Exposure of Automotive Compounds (D 1171-57T), 1957 Supplement to Book of ASTM Standards, Part 6, p. 248.

Based on quite a number of different rubber compounds, the authors have found that a reasonable degree of correlation of results exists between specimens set out for exposure in the summer and specimens tested in an ozone cabinet at 120° F, the cabinet being somewhat more severe. If the specimens were satisfactory in the cabinet, they were satisfactory outdoors; of those failing in the cabinet, about half still did not fail outdoors.

At 0° F, the correlation with outdoor winter exposures was not as good but still of some value; there was roughly a 2 to 1 chance that the outdoor specimens would duplicate the performance of the samples exposed in the ozone cabinet.

EFFECT OF COMPOUNDING VARIATIONS

It is well known that some rubbers may more easily be protected by wax than others. Figure 2 presents results on looped specimens of a number of rubber compounds to which a Sun Wax, Sunoco Anti-Chek, was added. The properties of Sunoco Anti-Chek are:

Melting point (cooling curve)	153° F
Penetration at 77° F	12
Penetration at 120° F	23
Saybolt viscosity at 210° F	43 sec

Formulas for the rubber compounds are given in Table I. The specimens were tested under both ozone and outdoor exposure conditions.

Formulas 1 and 2 (SBR and SBR plus reclaim) required only 3 parts per hundred parts rubber hydrocarbon (phr) of wax to protect against both 25 and 100 pphm of ozone at 120° F. For oil-extended SBR, 10 phr was needed; the accepted explanation is that the oil retains more of the wax in solution.

With SBR (Formula 1) and oil-extended SBR (Formula 3) 25 pphm ozone at 0° F was slightly less severe than at 120° F. This might also be attributed to the solubility effect, but with Formula 2 (SBR plus reclaim) 0° F was more severe than 120° F.

With natural rubber (Formula 4) more wax was required at 120° F to protect against 100 pphm than against 25 pphm. At 0° F only 1 phr was necessary.

Butadiene-acrylonitrile rubber (NBR) (Formula 5) and neoprene (Formula 6) are fully protected in the ozone chambers with 1 phr of wax.

The correlation between chamber tests and outdoor exposure was reasonably good. With natural rubber and NBR, however, more wax was required for complete protection than was indicated by the chamber tests. The outdoor samples of neoprene were recorded as failing in 329 days, but the failure appeared more of the type referred to as sun crazing than the typical ozone checking. This was confirmed by the fact that duplicate samples exposed in the same location for the same period, but in the shade, did not fail.

The data of Figure 2 show that the amount of wax must be adjusted to fit the formula, that conditions to be met must be kept in mind, and that accelerated tests must be supplemented by long-time exposures.

EFFECT OF DIFFERENT WAXES IN THE SAME FORMULA

Reference has been made to the variations in waxes. Not every wax added to a rubber compound will insure protection against ozone attack. The photo-

TABLE 1

FORMULATIONS FOR COMPOUNDS USED IN FIGURE 2

Formula 1
SBR passenger car tread stock

SBR 1500	100.0 Parts
Protox 166[a]	5.0 Parts
Santocure[b]	1.0 Part
Santoflex AW[c]	1.0 Part
Philblack O[d]	25.0 Parts
Philblack I[e]	25.0 Parts
Circosol 2XH[f]	10.0 Parts
Stearic acid	2.0 Parts
Sulfur	1.8 Parts
Wax A (Anti-Chek)	1 to 10 Parts

Cured 60 min at 292° F

Formula 2
Mixed SBR: Natural passenger car Sidewall stock

SBR 1004	100.0 Parts
Whole tire reclaim	25.0 Parts
Protox 166[a]	5.0 Parts
Captax[g]	0.8 Part
Diphenylguanidine (DPG)[h]	0.4 Part
B-L-E Powder[i]	0.75 Part
Micronex W-6[j]	25.0 Parts
Statex 93[k]	25.0 Parts
Circosol 2XH[f]	5.0 Parts
Stearic acid	1.0 Part
Sulfur	2.25 Parts
Wax A (Anti-Chek)	1 to 10 Parts

Cured 45 min at 292° F

Formula 3
Oil-extended rubber compound

SBR 1708	100.0 Parts
Protox 166[a]	5.0 Parts
Santocure[b]	1.0 Part
2246[b]	1.0 Part
Statex R[d]	50.0 Parts
Circosol 2XH[f]	5.0 Parts
Stearic acid	1.0 Part
Sulfur	1.8 Parts
Wax A (Anti-Chek)	1 to 10 Parts

Cured 45 min at 292° F

Formula 4
Natural heavy-duty truck tread stock

Smoked Sheet	100.0 Parts
Reogen[m]	2.0 Parts
Protox 166[a]	3.0 Parts
Altax[n]	0.75 Part
Akroflex CD[o]	1.0 Part
Micronex W-6[j]	45.0 Parts
Circosol 2XH[f]	2.0 Parts
Stearic acid	3.0 Parts
Sulfur	2.9 Parts
Wax A (Anti-Chek)	1 to 10 Parts

Cured 45 min at 272° F

Formula 5
NBR tubing extrusion

Hycar OR-15	100.0 Parts
Protox 166[a]	5.0 Parts
Age-Rite Resin D[p]	3.0 Parts
Altax[n]	3.0 Parts
Furnex[q]	100.0 Parts
Piccocizer[r]	15.0 Parts
Cumar P-25[r]	10.0 Parts
Stearic acid	0.5 Part
Ethyl Tuads[s]	2.0 Parts
Wax A (Anti-Chek)	1 to 10 Parts

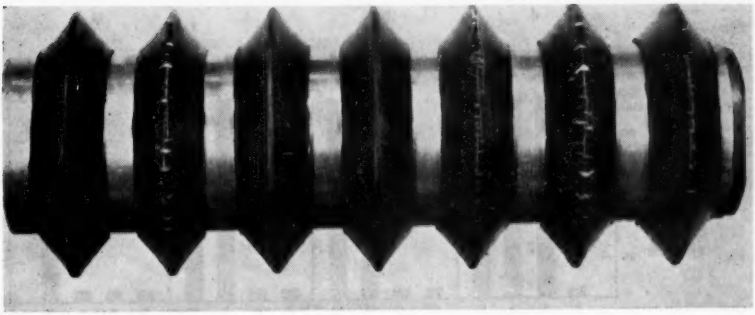
Cured 45 min at 307° F

Formula 6
Neoprene appliance wire

Neoprene W	100.0 Parts
Extra light MgO	4.0 Parts
Atomite[t]	75.0 Parts
Akroflex CD[o]	1.0 Part
Circo light Process Oil[u]	5.0 Parts
Protox 166[a]	5.0 Parts
NA-22[v]	1.5 Parts
Wax A (Anti-Chek)	1 to 10 Parts

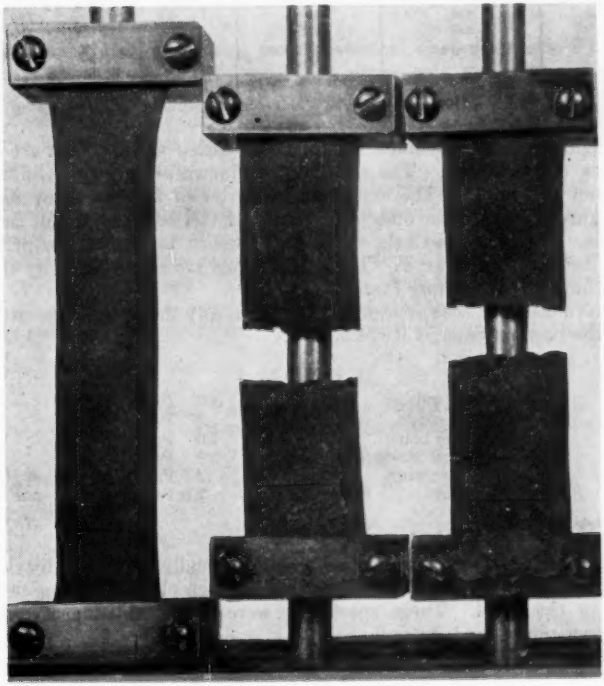
Cured 25 min at 307° F

[a] Trade name for propionic treated zinc oxide.
[b] Trade name for *N*-cyclohexyl-2-benzothiazolyl sulfenamide accelerator.
[c] Trade name for 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline antioxidant.
[d] Trade name for a high abrasion furnace black.
[e] Trade name for an intermediate super abrasion furnace black.
[f] Trade name for a medium viscosity naphthenic rubber processing oil.
[g] Trade name for mercaptobenzothiazole accelerator.
[h] Trade name for diphenylguanidine accelerator.
[i] Trade name for an antioxidant from a reaction product of diphenylamine and acetone.
[j] Trade name for an easy processing channel black.
[k] Trade name for a high modulus furnace black.
[l] Trade name for 2,2'-methylene-bis (4-methyl-6-*tert*-butylphenol) antioxidant.
[m] Trade name for a plasticizing agent from a mixture of sulfonic acids with oil.
[n] Trade name for benzothiazolyl disulfide accelerator.
[o] Trade name for diphenyl-*p*-phenylenediamine and *N*-phenyl-2-naphthylamine.
[p] Trade name for polymerized trimethyldihydroquinoline antioxidant.
[q] Trade name for a semireinforcing furnace black.
[r] Trade name for a polymerized aromatic resin plasticizer.
[s] Trade name for tetraethylthiuram disulfide accelerator.
[t] Trade name for calcium carbonate.
[u] Trade name for a low viscosity naphthenic rubber process oil.
[v] Trade name for 2-mercaptoimidazoline accelerator.



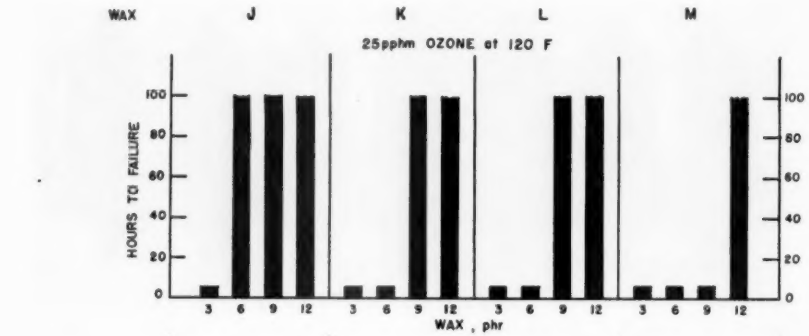
Wax A Wax B Wax C Wax D Wax E Wax F Wax G

FIG. 3.—Types of cracking encountered with different commercial waxes at 5 parts of wax per hundred parts of rubber used.



Wax A Wax H Wax I

FIG. 4.—Extremes in performance of anti-checking waxes in rubber at 4 parts wax loading.



	J	K	L	M
MELTING POINT F (COOLING CURVE)	158	161	157	159
PENETRATION 77 F	16	15	15	17
SAYBOLT VISCOSITY 210 F	527	504	45.4	47.8
ASSAY DISTILLATION AT 2mm Hg				
10 %	452	420	415	390
50%	536	530	475	504
FINAL	76% at 644 F	78% at 637 F	84% at 635 F	82% at 634 F

FIG. 5.—Difference in ozone protection of waxes having similar physical properties.

graph, Figure 3, shows a comparison of a half-dozen waxes which are sold for preventing ozone attack. The photograph illustrates the wide difference in behavior of the waxes. The extent and severity of failure varies markedly. In this figure, as well as the ones that follow, a letter code is used for the different waxes. Sunoco Anti-Chek, which was used in most of the experimental work, is designated as wax A. The other waxes are represented by the same letter if they appear in more than one test.

The formula used was representative of an automotive weatherstrip with SBR as the base polymer. It contained:

Formula 7

SBR rubber	100 Parts
Zinc oxide	3 Parts
HAF[a] black	50 Parts
Cumarone-indene resin	20 Parts
Accelerators	2.7 Parts
Sulfur	2.0 Parts

[a] High abrasion furnace.

The variation in behavior is even more dramatically illustrated by the specimens in Figure 4, where complete severing has taken place in two cases with no damage to the third. These specimens were compounded according to a typical mechanical goods formula.

THE ROLE OF WAX COMPOSITION

The difference in behavior of waxes must be due to variations in composition. Figure 5 gives the physical properties of four waxes, each a blend of paraffin

TABLE II

FORMULATION FOR COMPOUNDS USED IN FIGURE 5

Formula 8 SBR Automotive Weatherstrip	
SBR 1006	100.0 Parts
Zinc Oxide	3.0 Parts
Altax[a]	2.5 Parts
Ethyl Tuads[b]	0.15 Part
Philblack A[c]	54.0 Parts
Cumar MH 2½[d]	15.0 Parts
Cumar MS[d]	4.3 Parts
Sundex 53[e]	2.0 Parts
Sodium Acetate	0.5 Part
Sulfur	2.0 Parts
Wax	3 to 12 Parts
Cured 20 min at 300° F	

[a] Trade name for benzothiazolyl disulfide accelerator.
[b] Trade name for tetramethylthiuram disulfide accelerator.
[c] Trade name for a medium abrasion furnace black.
[d] Trade name for a polymerized aromatic resin plasticizer.
[e] Trade name for an aromatic rubber processing aid.

and microcrystalline waxes, and the results of chamber testing with 25 pphm of ozone at 120° F, using triangular specimens of SBR weatherstrip. (See Table II for the formula.)

The total spread of melting points is but 4° F; penetration, 2 points; and viscosity, about 7 sec. The distillation shows only moderate differences, including the material not distilled (18 to 24 per cent), which may be taken as an indication of the relative content of microcrystalline wax. Yet wax J provides full protection at 6 parts; waxes K and L at 9 parts; while wax M requires 12 parts.

It may therefore be concluded that it is impossible to predict the ability of a wax to protect rubber from ozone from an examination of the usual physical properties.

A number of commerical antichecking waxes were therefore subjected to more exhaustive analysis. Table III gives their physical properties. While the range of values is somewhat greater than for the waxes included in Figure 5, they still do not appear drastically different, although the double inflection

TABLE III

PHYSICAL PROPERTIES OF COMMERCIAL WAXES USED FOR OZONE PROTECTION

	Wax A	Wax N	Wax O	Wax P	Wax Q
Melting point, deg Fahr (cooling curve)[a]	154	147	141	165/143[b]	149
Penetration[c] at					
77° F	9	7	11	11	16
90° F	12	21	18	14	23
100° F	16	33			
110° F	21	56	56	37	90
120° F	29		200+	72	200+
130° F	43			200+	
Saybolt viscosity[d] at 210° F	45.1	46.5	41.6	51.1	53.3
Oil content[e], per cent by weight	0.1	0.1	0.2	0.8	1.7

[a] Sun method using constant differential cooling.
[b] Double inflection.
[c] ASTM Method D 5-52, 1955 Book of ASTM Standards, Part 3, p. 1643.
[d] ASTM Method D 446-53, 1955 Book of ASTM Standards, Part 5, p. 225.
[e] ASTM Tentative Method D 721-56T, 1956 Supplement to Book of ASTM Standards, Part 5, p. 303.

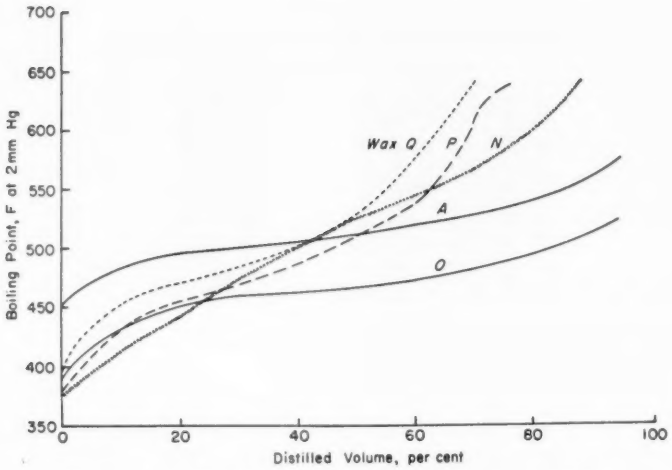


FIG. 6.—Vacuum distillation of commercial waxes used for ozone protection.

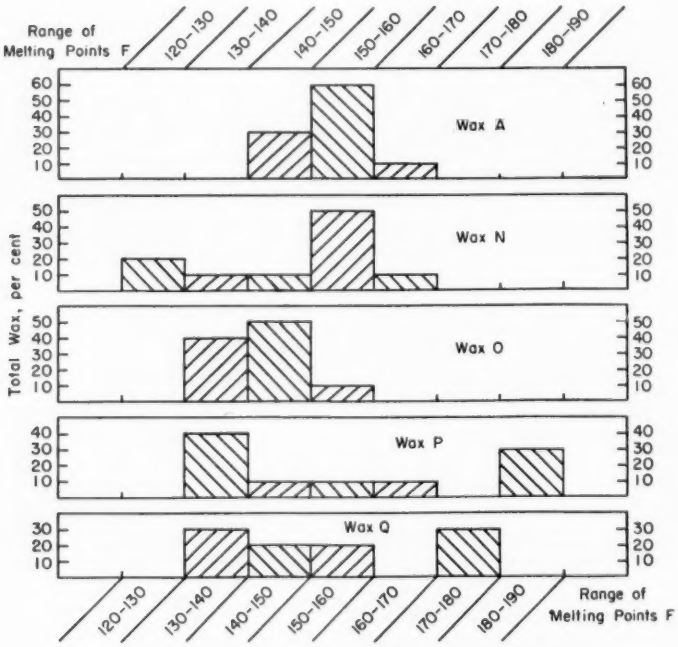


FIG. 7.—Melting point distribution of distillation fractions of commercial waxes used for ozone protection.

on the cooling durve of wax P suggests that it is a blend of paraffin and microcrystalline waxes.

The assay distillation curves (Figure 6) reveal that only A and O are paraffin waxes; the high-boiling portions of the others show the presence of microcrystalline wax, with the proportion increasing from N to P to Q.

Each wax was subjected to vacuum distillation, collecting 10 per cent distillate fractions and a residual fraction varying from 10 per cent to 30 per cent, depending upon the microcrystalline content, since microcrystalline waxes can be only partially distilled. Properties of each fraction were determined.

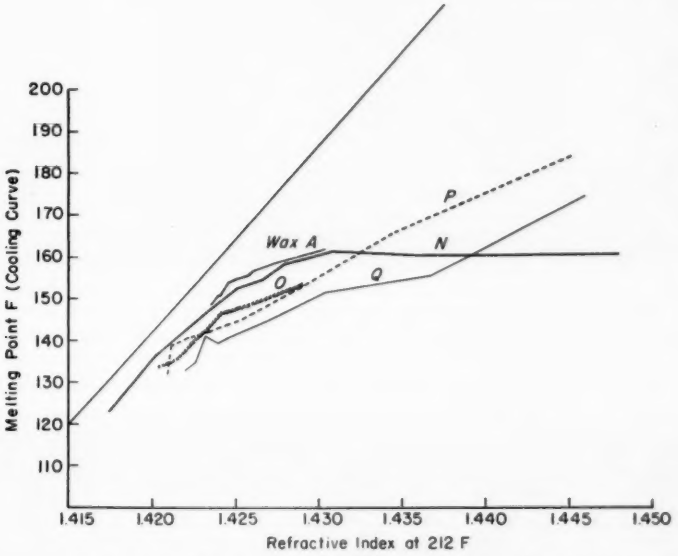


FIG. 8.—Refractive index relationship for distillation fractions of commercial waxes used for ozone protection.

Figure 7 shows the proportion of each wax, when so fractionated, which fell within the indicated melting point ranges. Considering all the waxes, the components extend, in melting point, from 120 to 190° F; some of the original waxes are of relatively narrow range and some of very broad range. Two of the waxes show "gaps," indicating that the waxes which were blended to form the antichecking wax were of widely different melting points.

Figure 8 shows both the melting point and the refractive index at 212° F of the same distillation fractions. The diagonal line at the left passes through the points for pure straight-chain paraffin hydrocarbons. Branched-chain paraffins lie to the right of this line; farther to the right lie cyclic and dicyclic hydrocarbons. Generally speaking, the more paraffinic components lie close to the normal paraffin line, while the other components discussed above are of the microcrystalline type.

It is immediately apparent that the differences in the waxes are not confined to the melting points of the constituents. Wax A is relatively high in

straight-chain paraffins; Q is rich in branched cyclic compounds. Wax N combines paraffinic low-melting fractions with medium-high-melting fractions rich in cyclic hydrocarbons. All of these waxes have been reported as giving satisfactory service, in spite of the great differences among them.

Figures 9 to 11 show results obtained on commerical waxes used for anti-checking at 6, 8, and 12 parts loading. The composition of these waxes is quite different.

Here again exposure results are affected by the loading for a particular wax. The compound in this case was a refrigerator door gasket containing both SBR and natural rubber as shown:

Formula 9

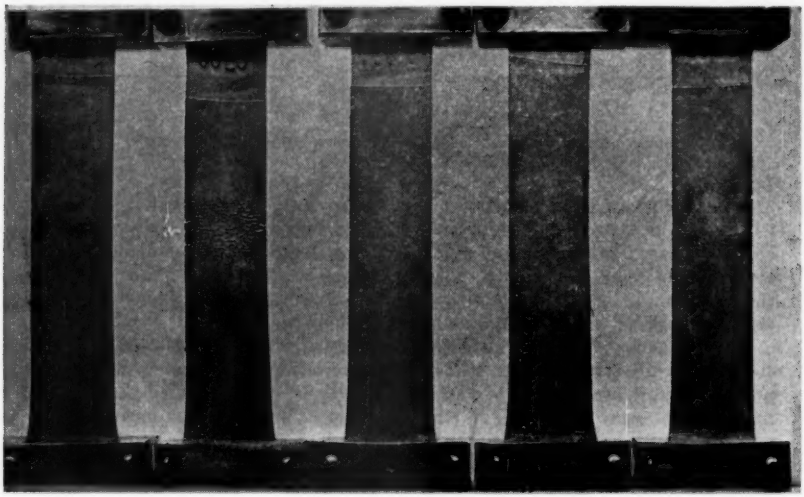
Natural rubber SBR	100 Parts
Zinc oxide	5 Parts
Clay	160 Parts
Accelerators	1.5 Parts
Sulfur	2.0 Parts

Figure 9 shows failure for all the waxes but one at a 6 parts loading.

Figure 10 shows continued failure for waxes R, E and S at 8 parts, but wax G is much better.

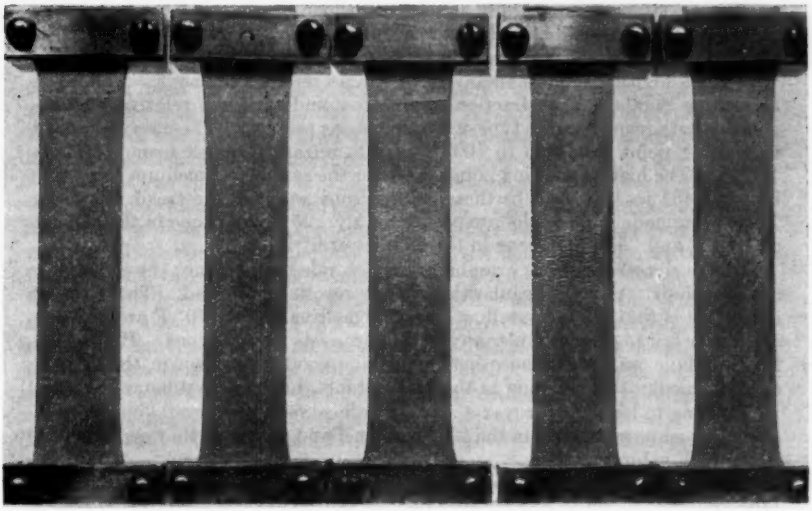
With 12 parts of wax (Figure 11), waxes G and R, as well as wax A, are protecting the compound. Wax E shows failure, and S slight failure.

In short, not only is it a mistake to assume that waxes of different composition will afford the same protection in rubber, but even with waxes of nearly the same physical properties there is no assurance that they will behave the same. It is seen that many different types of waxes are being marketed for anticheck-ing purposes. The results presented cast considerable doubt on the effective-ness of some of these waxes for this use.



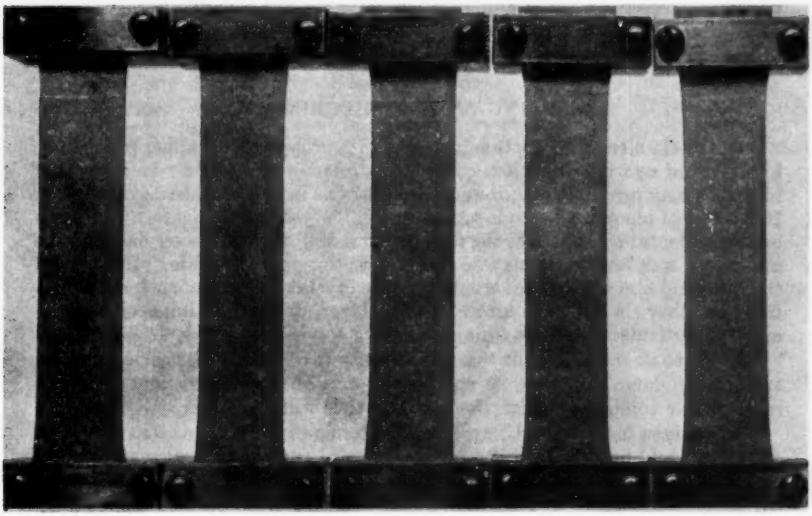
Wax A Wax G Wax R Wax E Wax S

FIG. 9.—Comparison of anti-checking waxes at 6 parts loading.



Wax A Wax G Wax R Wax E Wax S

FIG. 10.—Comparison and anti-checking waxes at 8 parts loading.



Wax A Wax G Wax R Wax E Wax S

FIG. 11.—Comparison of anti-checking waxes at 12 parts loading.

The question then naturally arises as to which of the many components of petroleum waxes should be included in an antichecking wax. Use was therefore made of a number of "research" fractions which had been fractionated to a very much higher degree than any of the waxes referred to above. The range of melting points in each fraction was narrow and each was relatively homogeneous with respect to the type of hydrocarbons present. These waxes ranged in melting point from 100 to 190° F and in refractive index from 1.4150 to 1.4555. The highest melting points were for the samples of medium refractive index (1.435 to 1.440). For these comparisons an SBR tire tread was used. Tests were made with outdoor exposure for 1 yr, 25 pphm ozone in the cabinet at 120° F and 25 pphm ozone in the cabinet at 0° F.

Of the sixteen fractions examined, five are microcrystalline; the remainder are paraffinic. Certain regularities in the results are found. The clearest indication is that microcrystalline fractions melting above 170° F are undesirable; they fail to protect under any of the three sets of conditions. High-melting paraffinic waxes, on the other hand, give good protection in the 120° F cabinet, moderate protection in the 0° F cabinet, but little outdoors.

Turning to low-melting waxes, both paraffins and microcrystallines behave similarly; while ineffective in the 120° F cabinet and outdoors, they are excellent in the 0° F cabinet.

The most interesting group consists of five paraffinic waxes melting between 140° and 150° F. The one melting just below 150° F comes closest to giving perfect results under all conditions tested, but the fraction just above it fails outdoors. The three near 140° F melting point are almost identical in their determinable properties. All are, chemically, paraffinic hydrocarbons, with the majority being normal—that is, straight chain. The differences can be only in minor differences in the proportions of branched hydrocarbons, or in the positions of such branches along the chain. Yet these small differences can result in the complete range of 0 to 3 ASTM rating at 120° F and 0 to 3 at 0° F in the ozone cabinet. All, however, are good in outdoor exposure.

TAILORING AN ANTICHECKING WAX

The mechanism of protection indicates that protection of rubber from ozone by means of wax involves close control of a number of factors. In order that blooming may proceed at all, the solubility of wax in rubber must be controlled. If the rate of blooming is too low, the film will be too thin to act as a barrier to ozone; if the rate is too high, the film will probably flake off in service, and the amount of wax remaining may be inadequate to replace the film. But even if the rates and film thicknesses are proper, the crystals may be of such configuration that they do not form an impervious layer, or even an impervious layer may be particularly subject to injury during service.

Added to all these difficulties is the inability to obtain precise correlation between reproducible laboratory conditions of rubber exposure and the nonreproducible conditions which the rubber article will encounter.

All of these factors can be explained in terms of the composition of waxes, or rather could be explained if our knowledge of composition were sufficiently complete, which unfortunately is not the case. It has been calculated for a paraffinic hydrocarbon of 25 carbon atoms (which is near the wax range) there may be 36,797,588 isomers[7]. The evidence of the 16 research fractions referred to suggests that performance on rubber may vary with such small changes in

molecular configuration that little or no differences can be found in determinable physical properties.

As a case in point, we manufacture two waxes that are essentially indistinguishable on the basis of physical tests; furthermore, they are completely interchangeable in all wax applications in which they have been tested except one, and that one is as an antichecking wax in rubber. The only differences are in the source of the crude wax from which the final wax fraction is recovered and slight modifications in refining procedures.

Under these circumstances, there is but one way to tailor an antichecking wax that can be reproducibly manufactured. Taking full advantage of information on different wax fractions, good waxes must be exhaustively compared in the laboratory and particularly in the field, in a variety of rubber formulations, to identify the excellent wax. Then every precaution must be taken to produce that wax in exactly the same way, from the same source materials. Until very much more is known about wax composition, it will be impossible to characterize an excellent antichecking wax so that it can be blended from readily available waxes. To specify, for example, a given percentage of paraffin of a given melting point, with a microcrystalline wax of stated melting point, amounts to essentially no specification at all. If one of the components of a successful blend is replaced by another which appears, in terms of physical properties, to be identical, unfortunate results may very well follow. Even more unfortunately, it may be only in the field, rather than in the ozone cabinet, where the tiny differences of composition will make their presence felt.

In summary, our experience with waxes used for protecting rubber from cracking leads us to believe that this field is more of an art than a science at the present time. Since we are unable to explain why one wax works so much better than another, we cannot too strongly emphasize that, having found a good wax by means of extensive laboratory and outdoor exposure, every effort must be made to insure that its quality is rigidly maintained.

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STRESS–STRAIN EQUATION FOR RUBBER IN TENSION *

W. E. CLAXTON

CHEMICAL AND PHYSICAL RESEARCH LABORATORIES, FIRESTONE TIRE AND RUBBER COMPANY, AKRON 17, OHIO

INTRODUCTION

Many advances have been made in the theory of rubberlike elasticity in recent years, especially along statistical lines[1]. However there is not, to the author's knowledge, a satisfactory stress-strain equation for large extensions which is readily applicable to the range of conventional physical testing data encountered in the study of various elastomers.

Attempts have been made by Hatschek[2], Ariano[3,4], Hencky[5], Mooney[6], and others[7] to obtain stress-strain relations for rubber that would be analogous to Hooke's law for elastic solids of low extensibility. Hatschek[2] concluded that stress-strain curves for rubber, when referred to attained cross section were rectangular hyperbolas. Ariano[3] experimentally evaluated Poisson's ratio as a function of extension and proceeded to derive stress-strain curves assuming them to be rectangular hyperbolas. Hencky[5] used a definition for finite tensile strain, wherein the strain was expressed as the natural logarithm of the ratio of the final to the initial length.

Perhaps best known is the work of Mooney[6], who obtained a strain energy function in terms of the principal elongations and arrived at a stress-strain curve involving two parameters. This two-parameter equation could be used to represent experimental data fairly well up to an extension of about 400%. To provide the rapid stress increase at higher extensions it was necessary to add a third term in the form of a constant times the elongation raised to some power.

An attempt was made by Leontein[8] to develop an empirical method for evaluation of various physical properties in terms of compound composition. Blackwell[9] has shown that existing stress-strain relations are inadequate to represent experimental data over a wide range of deformations and compounding variables. He also found the strain produced by a fixed load to be uniquely related to the load required for an elongation of 100%. Or, in other words, the experimental points in a plot of strain at 5 kg/cm^2 nominal stress vs. nominal stress at 100% elongation fell on a unique curve for all of the compounds tested. Blackwell concluded that all of the load-elongation curves studied could be expressed by a single type of basic equation, and that a single parameter representation would be possible. This conclusion is supported by the present work, in which applications to conventional physical testing data are suggested.

DERIVATIONS

In the classical theory of solid elasticity, the method of strain specification can be approached from an analogy to affine coordinate transformations leading

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to the classical strain tensor e_{ij}[10]. For a homogeneous, finite deformation the strain can be specified by the classical strain tensor, even though the principle of superposition is no longer valid for large deformations. Also, the method of specification of stress by means of the classical stress tensor can still be used for finite, homogeneous deformations. The inability of the classical theory of elasticity to yield correct stress-strain relations for homogeneous finite extensions must then be due to a breakdown of the relationship connecting stress and strain. In the case of the classical theory of solid elasticity the connecting relationship (Hooke's law) can be stated by[11]: the components of the stress tensor are to the first approximation, homogeneous, linear functions of the components of the strain tensor. This relationship between stress and strain leads to two elastic coefficients (C_{11}, C_{12}) for a homogeneous, isotropic material[10], both of which are normally assumed to be constants characteristic of the material. The classical connecting relationship between stress and strain can become invalid in two ways for finite homogeneous deformations: (a) the necessity of using higher order terms in the strain components (first approximation insufficient); (b) inconstancy of the elastic coefficients (C_{11} and/or C_{12} functions of the extension). The work of Murnaghan[12] on finite deformations copes with the first type of breakdown. It is shown below that C_{11} and C_{12} cannot both be constant if the sample volume remains fixed, which is approximately true for rubber. The stress-strain equation derived herein for rubber was obtained assuming inconstancy of the elastic coefficients as the reason for breakdown of the classical relationship connecting stress and strain for rubber in a finite homogeneous deformation.

In the notation of Sokolnikoff[10], the classical stress-strain relations referred to the principal axes for a homogeneous, isotropic material under a simple tensile strain are given by

$$\tau_{\mathrm{I}} = C_{11}e_{\mathrm{I}} + C_{12}e_{\mathrm{II}} + C_{13}e_{\mathrm{III}} \tag{1}$$

$$\tau_{\mathrm{II}} = C_{12}e_{\mathrm{I}} + C_{11}e_{\mathrm{II}} + C_{12}e_{\mathrm{III}} = 0 \tag{2}$$

$$\tau_{\mathrm{III}} = C_{12}e_{\mathrm{I}} + C_{12}e_{\mathrm{II}} + C_{11}e_{\mathrm{III}} = 0 \tag{3}$$

where τ_{I} is the applied stress, e_{I} is the extension in the direction of stretching, and C_{11} and C_{12} are elastic coefficients. If one substitutes $e_{\mathrm{II}} = e_{\mathrm{III}} = -\sigma e_{\mathrm{I}}$ in the above equations, where Poisson's ratio

$$\sigma \equiv |e_{\mathrm{II}}|/|e_{\mathrm{I}}| = |e_{\mathrm{III}}|/|e_{\mathrm{I}}|$$

either of the last two equations can be solved for C_{11} in terms of σ and C_{12}, yielding: $C_{11} = [(1/\sigma) - 1]C_{12}$. Hence, the applied stress τ_{I} can be written as

$$\tau_{\mathrm{I}} = [(1/\sigma) - (2\sigma + 1)]C_{12}e_{\mathrm{I}} \tag{4}$$

In classical elasticity theory, both σ and C_{12} are considered constant for infinitesimal deformations and the above equation is a form of Hooke's law in this case. On the case of finite deformations and a material such as rubber whose volume remains essentially constant upon stretching, it is readily shown that

$$\sigma = (1/e_{\mathrm{I}})[1 - (1 + e_{\mathrm{I}})^{-\frac{1}{2}}] \tag{5}$$

as a result of a constancy of volume restriction. Hence, one would expect the above stress-strain equation to hold with σ a known function of e_1 for a finite homogeneous tensile strain, or

$$\tau_1 = C_{12}\Phi(e_1) \tag{6}$$

where $\Phi(e_1)$, is a known function of e_1 given by

$$\Phi(e_1) = [(1/\sigma) - (2\sigma + 1)]e_1$$

As derived τ_1 represents the applied stress referred to the original cross-sectional area.

TABLE I

STOCK FORMULAS

Stock	*A*	*B*	*C*	*D*	*E*-1 to *E*-6	*F*-1 to *F*-6	*G*-1,2,3	*H*-1,2,3	*I*-1,2,3	*J*-1,2,3	*K*-1,2,3
Hevea		100	100				100	100	100	100	100
LTP				100	100	100					
BD/MMA	100										
SAF black							10,35,60				
HAF black	30				10,20,30 40,50,60			10,35,60			
EPC black			40	30		10,20,30 40,50,60			10,35,60		
MT black										10,35,60	
Whiting											10,35,60
Zinc oxide	4.0	4.0	3.0	4.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Stearic acid	10.8	1.5	10	1.5	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Bardol	4.0										
Paraflux							3.0	3.0	3.0	3.0	3.0
Circosol 2XH					8.0	8.0					
Pine tar	4.0										
Resin	4.0										
PBNA					0.6	0.6					
Sulfur		3.0	2.0	3.0	2.0	2.0	2.25	2.25	2.25	2.25	2.25
Insol. sulfur	3.0										
Santocure					1.2	1.2	0.35	0.35	0.35	0.35	0.35
MBT			1.0								
DBAO	0.77	0.7		0.7							
MBTS	1.1	1.6		1.6							
Retarder W							1.0	1.0	1.0	1.0	1.0

Stock	*L*	*M*
Hevea		100
LTP	100	
EPC black	45	50
Zinc oxide	2.4	3.0
Stearic acid	2.5	3.0
Bardol	4.0	
Paraflux	2.6	4.0
PBNA	0.6	
Santocure	1.0	
Sulfur	2.0	

Explanation of compounding terms used:

LTP—low-temperature polymer (GR-S-1500)
BD/MMA—butadiene/methylmethacrylate copolymer
SAF—super abrasion furnace carbon black
HAF—high abrasion furnace carbon black
EPC—easy processing channel carbon black
MT—medium thermal carbon black
Whiting—calcium carbonate pigment
Bardol—refined coal tar fraction (Barrett Division, Allied Chemical Company & Dye Corporation)
Paraflux—petroleum processing oil (C. P. Hall Company)
Circosol 2XH—petroleum processing oil (Sun Oil Company)
Resin—light colored rosin
PBNA—phenyl-2-naphthylamine
Ajone C—Santoflex B (Monsanto Chemical Company)
Santocure—*N*-cyclohexyl-2-benzothiazolesulfenamide
MBT—2-mercaptobenzothiazole
DBAO—bibutyl ammonium oleate
MBTS—benzothiazolyl disulfide
Retarder W—salicylic acid

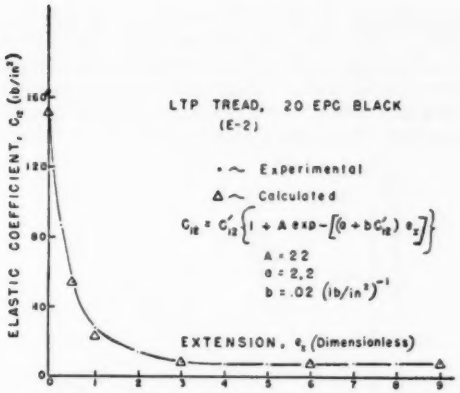

FIG. 1.—Experimentally established dependence of elastic coefficient C_{12} on strain.

RESULTS

In the applications that follow, stock formulations can be determined by referring the letter accompanying each figure or table to the stock formulas given in Table I.

Table IV shows computed values for σ and $\Phi(e_I)$ for various values of e_I. Experimental values of the stress were divided by $\Phi(e_I)$ and several plots of C_{12} as a function of e_I similar to that shown in Figure 1 were obtained. For the Hevea and LTP stocks investigated the average dependence of C_{12} upon extension could be approximated by

$$C_{12} = C_{12}'[1 + A \exp(-ae_I)] \tag{7}$$

The constants A and a are found to vary for different stocks. Average values for the stocks investigated gave values $A = 22$ and $a = 2.2 + 0.02\ C_{12}'$, wherein C_{12}' is a constant and is dependent upon black loading, cure, etc. In the cases investigated it was found that for all practical purposes $C_{12} = C_{12}'$ for extensions greater than 250%. This approximation is valid at much lower extensions for stiff stocks ($C_{12}' > 100$ lb/in.^{2}) as is indicated by the above equation for C_{12}. The nature of the dependence of C_{12} upon extension might be interpreted in the following manner: the elastic coefficient depends upon contributions from both primary and secondary bonds. The effectiveness of the secondary bonds increases with the number of primary bonds (C_{12}'), and decreases with increasing extension becoming negligible above 250% extension. The primary bonds referred to here would be the crosslinking chemical bonds (sulfur to carbon) whereas the secondary bonds would include physical forces such as van der Waals' forces. Figure 2 shows a plot of Equation (4) for a very soft, a medium, and a very stiff rubber compound using values for the constants A and a as given above.

As already mentioned, Equation (4) in the foregoing with σ and C_{12} constant is merely an expression of Hooke's law. This equation predicts that an isovolumetric material ($\sigma = \frac{1}{2}@e_I = 0$) would have a Young's modulus equal to

zero if C_{12} remains finite. If C_{12} is allowed to go to infinity, then the shear modulus $\mu = \frac{1}{2}(C_{11} - C_{12})$ becomes zero since $C_{11} = C_{12}[(1/\sigma) - 1]$. These are properties of a fluid and may be of philosophical significance as regards the behavior of rubber at zero strain. The viscous stress component which is present in rubber with any finite rate of stretching probably complicates experimental determinations of the truly elastic behavior of rubber at zero strain.

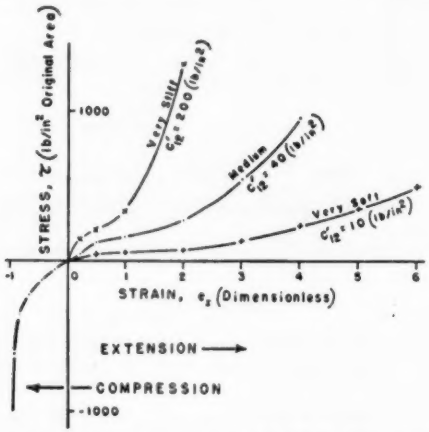

FIG. 2.—Calculated stress-strain curves for a range of values of the parameter C_{12}' [calculated using Equation (4) and average values in the relationship (7)].

In order to obtain a working equation that would agree with experimentally found slope values of the stress-strain curve at the origin, one could use in lieu of Equation (7) an approximation of the form

$$C_{12} = C_{12}'[1 - B \exp(-be_I)]^{-1}$$

This equation would permit C_{12} to approach infinity with $1/e_I$ as zero strain is approached and with proper choice of the constants B and b would still permit $C_{12} \rightarrow C_{12}'$ for extensions of 250% or greater.

The equation

$$\tau_I = [(1/\sigma) - (2\sigma + 1)]C_{12}'e_I \tag{8}$$

where C_{12}' = constant, was found to agree quite well with conventional physical testing data (stress at extensions of 250% and greater) obtained on a Scott tensile machine over a wide range of curing times and for a large variety of compounds. Figure 3 shows the extent of this agreement for a butadiene-methyl methacrylate copolymer stock. The constant C_{12}' was found to increase with curing time according to an equation similar to that reported by Blackwell and others[13]:

$$C_{12}' = C_{12}^0\{1 - \exp[-k(t - t_0)]\} \tag{9}$$

where C_{12}^0 = limiting value of C_{12}' as t increases, k = curing rate constant, t = molding time, and t_0 = induction period. In practical agreement with

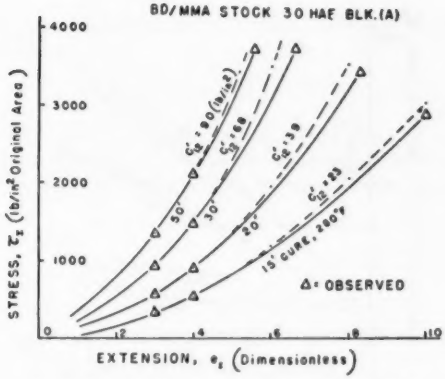

FIG. 3.—Agreement between conventional physical testing stress-strain data and theoretical curves using Equation (8) (C_{12}' = constant) for a range of cures.

these authors and in accord with recent publications describing the curing reaction in filler-reinforced stocks[14] the ratio C_{12}'/C_{12}^0 appears to be a logical definition of state of cure. This ratio with aceptance of the foregoing stress-strain equations is independent of the extension. This ratio was found to be linearly related to crosslinking as determined from swelling measurements for a Hevea gum stock and for a Hevea and a LTP black loaded stock. The crosslinking by swelling data were furnished by H. E. Adams using the technique described in the paper by Adams and Johnson[15] and are shown in Figure 4.

The constant C_{12}^0 was found to increase linearly with the square of the volume fraction of reinforcing pigment for a Hevea stock, as is shown by the data in Figure 5. The slopes of the straight lines in this plot are a measure of the reinforcing properties of the various pigments. Similarly, slope values of 1800 and 2900 lb/in.² were found for EPC and HAF blacks, respectively, in a SBR stock.

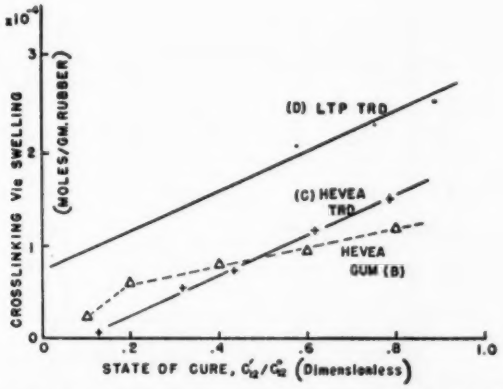

FIG. 4.—Crosslinking by swelling measurements vs. fractional modulus state of cure.

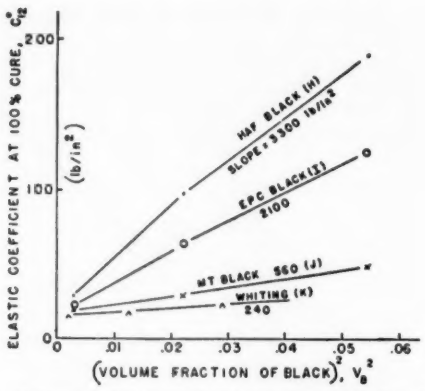

FIG. 5.—Dependence of fully cured elastic coefficient C_{12}^0 on type and loading of reinforcing pigment.

Physical testing data for a SBR and a Hevea compounded stock over a range of curing temperatures from 262 to 316° F showed that changing the curing temperature had very little effect on the constant C_{12}^0 the trend being, if real, in the direction of slightly smaller values (order of 10%) at the highest curing temperatures.

The effect of curing temperature on the rate constant k and the induction period t_0 is shown in Figure 6. From reaction rate theory and the Arrhenius equation,

$$k = A \exp(-E/R\theta), \text{ (where } E \text{ is activation energy, } R \text{ the gas constant, and } \theta \text{ the absolute temperature)} \quad (10)$$

an activation energy of about 20 kcal/mole was evaluated from this plot for the crosslinking reaction in both the Hevea and SBR stocks. The induction period (molding time before modulus starts increasing significantly) t_0 is known to depend upon the thermal history of a stock, hence it might be supposed that

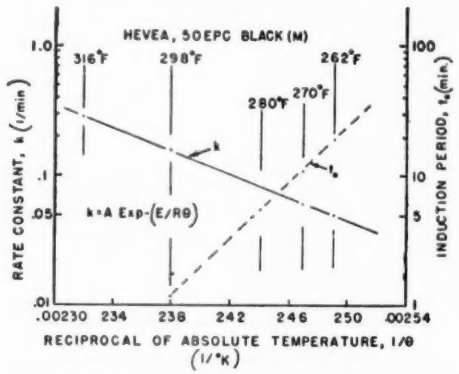

FIG. 6.—Dependence of curing rate constant k and induction period t_0 on curing temperature.

crosslinking commences instantaneously at time $t = 0$ and proceeds according to a first-order reaction:

$$X = X_\infty[1 - \exp(-Kt)] \tag{11}$$

wherein X represents crosslinks/unit volume. This assumes that compounds which will react with polymer to produce cure are all present at the start of cure, whereas some might be formed from decomposition of accelerator, etc.

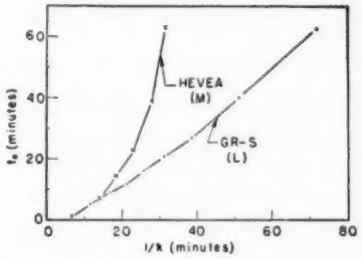

FIG. 7.—Induction period t_0 vs. reciprocal of curing rate constant $(1/k)$ with curing temperature varied.

With the above assumption at time t_0 there would have been formed a number of crosslinks X_0 given by

$$X_0 = X_\infty[1 - \exp(-Kt_0)] \tag{12}$$

virtually ineffective in increasing the modulus of the stock. Upon solving for the induction period, one obtains

$$t_0 = (1/K)\log_e\{1/[1 - (X_0/X_\infty)]\} \tag{13}$$

The ratio (X_0/X_∞) should be reasonably independent of curing temperature hence if curing temperature alone were varied the above equation would predict a straight line relationship for t_0 vs. $1/K$. If it be assumed that C_{12}' increases with crosslinking in excess of the amount X_0 namely $C_{12}' \propto (X - X_0)$, then by comparing the equations

$$(X - X_0) = (X_\infty - X_0)\{1 - \exp[-K(t - t_0)]\} \tag{14}$$

and

$$C_{12}' = C_{12}^0\{1 - \exp[-k(t - t_0)]\} \tag{9}$$

one would conclude that $k \equiv K$ and a straight line relationship would be expected for the plot t_0 vs. $1/k$ where only the curing temperature is varied. Figure 7 shows such a plot for the Hevea and SBR stocks. The SBR stock gave a reasonably linear plot over the full range of curing temperatures employed. Evaluation of the ratio X_0/X_∞ at the 280° F cure yields a value of about 0.65 for the SBR stock, which with the above interpretation would indicate that 65% of the total number of crosslinks possible are formed before the modulus starts increasing. The same ratio for the Hevea stock at 280° F was

evaluated as 36%. The reason for the nonlinearity in the Hevea plot is not known. Since the ratio at hand is given by: $X_0/X_\infty = [1 - \exp(-kt_0)]$, it appears that this ratio becomes larger at lower curing temperatures for the Hevea stock. Conceivably then, one could interpret the curvature as indicating that if the crosslinks are formed more slowly, a greater number will be formed before the modulus starts increasing in the case of the Hevea stock. It is presupposed in this analysis that there is no induction period associated with the reactivity of the accelerator or other compounding ingredients.

From an analysis of the above type one could also relate the modulus unsaturation to the crosslink unsaturation by the equation

$$(1 - C_{12}'/C_{12}^0) = (1 - X/X_\infty) \exp(kt_0) \tag{15}$$

Such a relationship might prove useful in establishing comparable degrees of cure for SBR and Hevea stocks based on modulus vs. cure time data. For example the 280° F cure for the data at hand would indicate that for 90% cross-

TABLE II

OBSERVED AND CALCULATED CURE FOR MAXIMUM TENSILE

	Minutes at 280° F					Minutes at 280° F			
	45	60	90	120		45	60	90	120
10 HAF (*E*-1)					40 HAF (*E*-4)				
Cure	0.33	0.47	0.80	0.90		0.49	0.71	0.90	0.98
Calculated cure for max tensile		0.43						0.95	
Observed tensile (lb/in.²)	925	960	370	550		2975	3000	3150	3130
20 HAF (*E*-2)					50 HAF (*E*-5)				
Cure	0.41	0.61	0.82	0.97		0.57	0.71	0.89	0.97
Calculated cure for max tensile			0.72						1.0
Observed tensile (lb/in.²)	1760	2600	2210	2100		2925	3200	3300	3400
30 HAF (*E*-3)					60 HAF (*E*-6)				
Cure	0.39	0.73	0.93	0.98		0.60	0.75	0.90	0.97
Calculated cure for max tensile			0.75					0.88	
Observed tensile	2412	3175	2700	2250		2850	3200	3300	3275

Observed tensile values are from conventional physical testing data. Calculated cures for maximum tensile computed using Equation (16).

link saturation the Hevea stock should be cured to 85% modulus saturation whereas the SBR stock should be cured only to 82% modulus saturation.

Excluding very low cures, the ultimate elongations of Hevea and SBR stocks appear to decrease linearly with an increase in the ratio C_{12}'/C_{12}^0. Using such a straight line relationship for the ultimate elongation (experimentally established), differentiation of the stress-strain Equation (8) with respect to the degree of cure explicitly expressed therein, a predicted cure for maximum tensile can be obtained, which is given by the equation

$$K_{max} = \frac{0.35}{m}(e_j + mK_j) \tag{16}$$

in which m is the absolute value of the slope of the ultimate elongation vs. cure plot, e_j is the ultimate elongation at cure K_j where $0 \leq K_j \leq 1.0$. The data in Table II indicate rather good agreement between predicted and observed cures for maximum tensile for an LTP stock with various loadings of HAF black. The data in this table support the theory that the ultimate elongation of a given

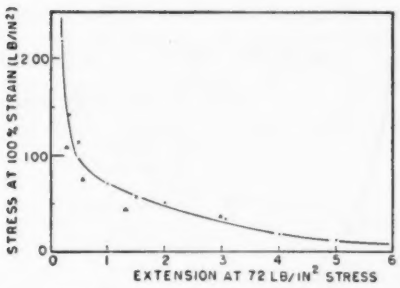

FIG. 8.—Stress at 100% extension vs. extension at 72 lb/in.² (5 kg/cm²) stress. Calculated; × data from Reference 13; Δ experimental.

stock is determined by the state of cure (degree of crosslinking) and that the commonly observed optimum in tensile values as cure time progresses is not necessarily due to unusual behavior of the material (reversion, crystallization, volume change, etc.), but is a consequence of the peculiar stress-strain relationship together with the dependence of ultimate elongation on crosslinking.

The derived stress-strain relationship also predicts a unique curve for stress at constant strain vs. strain at constant stress as predicted by Blackwell[9]. Figure 8 shows the computed curve in the case of a given stress of 72.4 lb/in.² (5 kg/cm²) and a given strain of 100% extension. Some of the experimental points were taken from the data reported by Blackwell[9] and are seen to be in close agreement with the computed curve. Figure 9 is a similar plot relating 300% modulus to the strain at 462.5 lb/in.² stress. The experimental modulus values shown are from conventional physical testing data.

Using the stress-strain Equation (4) derived for low extensions (C_{12} a function of extension) and the observed dependence of C_{12}' on curing time, Equation 9, the strain at constant load (100 lb/in.²) was computed as a function of curing time. The resultant curve (Figure 10) could be approximated quite closely by a hyperbolic type equation as proposed by Stiehler and Roth[16] and further developed by Schade[17]. Hence, it would appear that the vulcanization reaction could be characterized by either a hyperbolic equation giving strain at constant load as a function of curing time or by an exponential (natural growth) type equation relating the elastic coefficient C_{12}' to the curing time.

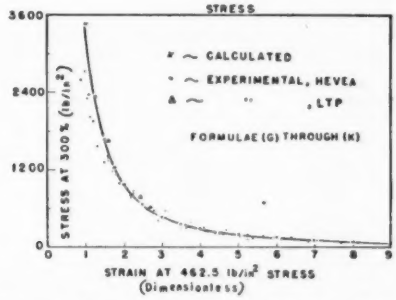

FIG. 9.—Stress at 300% extension vs. extension at 462.5 lb/in.² stress.

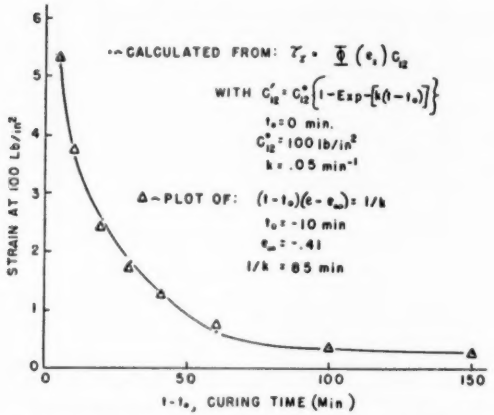

FIG. 10.—Computed behavior of strain at constant stress as a function of cure time.

The latter procedure appears to give cure parameters which are more easily interpreted and perhaps have more physical significance than in the case of the former procedure. Working with relative modulus values as a function of curing time the induction period is definitely that cure time for which the modulus commences increasing rapidly and the rate constant k is typically a first-order reaction rate constant.

Inasmuch as C_{12}' is proportional to any given conventional secant modulus for extensions greater than 250%, an exponential type equation would also apply to secant modulus as a function of curing time provided a modulus of 250% or greater were used. In order to measure state of cure from strain at constant load data, in agreement with the definition C_{12}'/C_{12}^0, the ratio ψ/ψ_0 should provide the closest agreement where

$$\psi(e_1) = 1/\Phi(e_1) = \{[(1/\sigma) - (2\sigma + 1)]e_1\}^{-1} \qquad (17)$$

and ψ_0 is the limiting value of ψ as curing time progresses. This ratio is applicable, provided the strain e_1 produced by the constant load is greater than 250%.

TABLE III

COMPARISON OF STATE OF CURE BY STRAIN AT CONSTANT LOAD METHOD AND BY MODULUS METHOD (HEVEA STOCK, 35 EPC, (I)][a]

Cure at 280° F (minutes)	Strain at constant load, e_1	ψ/ψ_0	300% modulus lb/in.²	C_{12}'/C_{12}^0
25	3.60	0.34	325	0.34
35	2.85	0.52	550	0.58
60	2.25	0.82	800	0.84
90	2.15	0.89	910	0.95
120	2.05	0.97	925	0.97
$\rightarrow\infty$	$\rightarrow$2.00	$\rightarrow$1.00	$\rightarrow$950	$\rightarrow$1.00

[a] Modulus measurements were from Scott tensile machine using conventional test procedure (strain rate about 20%/sec). Strain measurements were made using ¼-inch wide by 0.075-inch thick dumbbell strips from ¼-inch benchmarks thereon. Load was 8.65 lb (462.5 lb/in.² stress), rate of load application was controlled, giving a strain rate about 5 times that employed in the Scott machine. Creep was controlled by holding the separation between clamps constant from 2 seconds after the sample supported the full load.

Actually, this ratio can be used at lower extensions in the case of high modulus stocks since $C_{12} \rightarrow C_{12}'$ at extensions much less than 250% for these stocks. Some values of the function ψ are shown in Table I from which a continuous plot can be made for evaluation purposes if desired. The extent of agreement for state of cure obtained by the two methods in the case of a Hevea stock compounded with 35 parts EPC black per 100 parts rubber hydrocarbon is shown in Table III.

TABLE IV

COMPUTED VALUES OF FACTORS TO FACILITATE USE OF THE STRESS–STRAIN EQUATION

e_I	σ	$\Phi(e_I)$	$\psi(e_I)$
0.000	0.500	0.000	—
0.100	0.465	0.0221	—
0.200	0.436	0.0843	—
0.300	0.409	0.189	—
0.400	0.387	0.324	—
0.500	0.367	0.495	—
0.600	0.349	0.700	—
0.700	0.333	0.933	—
0.800	0.318	1.21	—
0.900	0.305	1.50	—
1.00	0.293	1.83	—
1.25	0.267	2.76	—
1.50	0.245	3.89	0.257
1.75	0.227	5.16	0.194
2.00	0.211	6.63	0.151
2.50	0.186	10.0	0.100
3.00	0.167	14.0	0.0716
3.50	0.151	18.6	0.0537
4.00	0.138	23.9	0.0419
4.50	0.127	29.8	0.0336
5.00	0.118	36.2	0.0276
5.50	0.111	42.8	0.0234
6.00	0.104	50.4	0.0198
7.00	0.0923	67.5	0.0148
8.00	0.0833	86.7	0.0115
9.00	0.0760	108	0.00926
10.0	0.0698	132	0.00757
12.0	0.0602	186	0.00538
14.0	0.0530	249	0.00402

$$\tau = \Phi(e_I)C_{12} \qquad \sigma = (1/e_I)[1 - (1 + e_I)^{-\frac{1}{2}}]$$

$$\Phi(e_I) = [(1/\sigma) - (2\sigma + 1)]e_I \quad \psi(e_I) = 1/\Phi(e_I)$$

CONCLUSIONS

The first stretch stress-strain equation $\tau_I = C_{12}\Phi(e_I)$ was derived for an isotropic, iso-volumetric material where $\Phi(e_I) = [(1/\sigma) - (2\sigma + 1)]e_I$ and Poisson's ratio $\sigma = (1/e_I)[1 - (1 + e_I)^{-\frac{1}{2}}]$. For a wide variety of rubber compounds and cure conditions C_{12} was found to be essentially equal to a constant C_{12}' for extensions above 250%. For lower extensions it appears that C_{12} is expressible in terms of C_{12}'. The average relationship

$$C_{12} = C_{12}'\{1 + 22 \exp [-(2.2 + 0.02C_{12}')e_I]\}$$

proved fairly successful in representing the stress-strain curves of the compounds used down to extensions of 25%.

The fact that the elastic coefficient increases at lower extensions can be interpreted as due to secondary bonds, the effective number of which becomes quite large at low extensions. This agrees generally with the work of Blanchard and Parkinson[18] on the distribution of bond strengths.

The derived stress-strain equation is concerned only with the elastic component of the stress, hence for best agreement stress measurements should be made after allowing the viscous stress component to decay. For extensions greater than 250%, a 15-second relaxation appears adequate. The equation has been applied successfully using normal physical testing procedures however (strain rate small, order of 20% per second), wherein C_{12}' was evaluated directly from any chosen secant modulus greater than 250% extension (see Table IV).

The elastic coefficient C_{12}' was found to increase with curing time t according to the equation

$$C_{12}' = C_{12}^0\{1 - \exp[-k(t - t_0)]\}.$$

The limiting value of C_{12}' as cure increases, C_{12}^0, was found to increase linearly with the square of the volume fraction of reinforcing pigment in the compound. The slope of the straight line thus obtained was taken as an index of modulus reinforcement for the pigment. The ratio C_{12}'/C_{12}^0 was assumed to be a practical measure of the state of cure and was shown to be approximately proportional to the degree of crosslinking in a vulcanizate. Ultimate elongation was found to decrease in a linear fashion with an increase in this ratio. The commonly observed optimum in tensile strength as cure time progresses can usually be attributed to the opposite dependence of ultimate elongation and elastic coefficient on cure time together with the peculiar stress-strain equation for rubber as reported herein.

A unique curve is predicted between stress at constant strain and strain at constant stress as has been indicated by Blackwell[9]. Good agreement between the theoretical and experimental curves was obtained. In the present work it is indicated that the cure curve can be represented by either a hyperbolic type equation involving strain at constant load data[17] or the above-mentioned increasing exponential (or natural growth) curve involving the elastic coefficient. Values for a function $\psi(e_1)$ are given in Table IV which should enable percentage cure to be evaluated rapidly from strain at constant load data in agreement with that evaluated from elastic coefficient (or modulus) data.

One interpretation of the induction time that is normally observed before cure commences leads to the conclusion that a certain percentage of the total number of crosslinks must be formed, depending upon the type of compound, before the modulus starts increasing significantly. This interpretation leads to the requirement of slightly different modulus saturations to obtain the same crosslink saturations in the Hevea and SBR stocks investigated.

The derived equation has been successfully applied to: (a) gum stocks of styrene/butadiene rubber and of Hevea rubber (C_{12}' of the order 2 to 10 lb/in.^{2}); (b) Hevea stocks with various loadings of inert filler (C_{12}' of the order 10 to 15 lb/in.^{2}); (c) Hevea and styrene/butadiene rubber stocks with various loadings of different reinforcing carbon blacks (C_{12}' of the order of 10 to 200 lb/in.^{2}); (d) compounded stocks from various types of polymers such as butyl, butadiene/methylmethacrylate copolymer, nitrazole-CF, butaprene, and others (C_{12}' of the order 10 to 250 lb/in.^{2}). Fair agreement was obtained between experimental and the derived stress-strain curve for the above stocks over wide ranges of

elongations up to breaking elongations except for the natural rubber gum stocks. These showed a much more rapid increase in stress at around 600% extension than predicted by the stress-strain equation (C_{12}' evaluated at 300%) which undoubtedly was due to the onset of crystallization. In unpublished work by W. A. Smith of the Firestone Chemical and Physical Research Laboratories, the crystallizing behavior of various polymers has been compared by evaluating the stress enhancement relative to the predicted stress-strain curve for various extensions.

There has also been observed evidence for vacuole formations in butadiene/styrene stocks compounded with the weaker reinforcing carbon black at elongations near break. This behavior is evidenced by a rather abrupt departure to experimental stress values less than predicted by the stress-strain equation near the breaking elongation.

It is believed that the present work should elucidate several interesting aspects of stress-strain and cure behavior of rubber and that the derived equation could serve as a starting point in any detailed investigation of various anomolies such as small volume changes which do occur experimentally[19], viscous forces, plastic flow, and crystallization effects which were not accounted for in the present work.

SUMMARY

A stress-strain equation is derived for a homogeneous, isotropic material with the assumptions that for any given homogeneous simple tensile strain, the components of the stress tensor are to the first approximation linear, homogeneous functions of the components of the strain tensor and that no volume change occurs during the deformation. Utilizing the dependence of Poisson's ratio upon the extension referred to the initial coordinates, one elastic coefficient, C_{12}, is found to be sufficient to roughly characterize the first stretch stress-strain curve. Although experimentally this elastic coefficient is found to be essentially constant for extensions greater than 250% its value increases rapidly as zero extension is approached. This behavior agrees qualitatively with data by Blanchard and Parkinson as to the distribution of secondary bond strengths, wherein they found a large number of relatively low-energy bonds which would be effective only at small extensions in contributing to modulus reinforcement. Various aspects of stress strain and cure behavior are examined with the derived equation as a basis.

ACKNOWLEDGMENTS

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STRESS-STRAIN RELATION IN RUBBER BLOCKS UNDER COMPRESSION. I *

GÉZA SCHAY AND PÉTER SZÖR

CENTRAL RESEARCH LABORATORY OF THE RUBBER INDUSTRY, BUDAPEST, HUNGARY

One of the prerequisites of correct dimensioning of rubber springs is the exact knowledge of the stress-strain relation. Rubber springs are liable to be subjected to compression, shear and torsion. It has been found that the stress-strain curve is in general greatly dependent on the shape of the rubber spring, but independent of its absolute dimensions, so that geometrically similar bodies behave in the same manner. In the present paper we intend to deal with compression only. Until now only a limited series of experiments and tabulated values derived therefrom are available as to the shape of the stress-strain curve[1], whereas their theoretical coordination has not been made yet. In the following we shall put forward an equation by which these curves can be calculated on a uniform basis, provided we know the shear modulus of the rubber substance and only one experimental constant which depends solely on the shape of the rubber block and may be determined by a single measurement.

We are concerned with the only case of practical interest, when the compression of the rubber block is effectuated by a stress acting upon two parallel faces of the block, these faces being fixed to the solid surfaces in contact with them (metal fittings) in a way that no slip can occur. Under these conditions these surfaces remain unchanged at any degree of compression. The deformation of the block, consequently, manifests itself only at the free sides and, as experience shows, is always accompanied by an increase of the area of these surfaces, at least in the case of block-shapes and strains of practical interest. The reason for this increase lies in the fact that the volume of the rubber remains practically unchanged even when compressed to the greatest extent occurring in practice[2], that is, the block gives way to the applied stress only by a change of its form. This is one of the main differences between the elastic behavior of rubber and that of normal elastic solids. The other important difference is, that with normal solids the yield point confines the range of elastic deformations to very small values, whereas rubber blocks can be compressed in a completely elastic manner to a relatively small fraction of their original height. Consequently Hooke's proportionality law cannot be applied in the case of rubber, the stress increasing more rapidly than the deformation.

The statistical theory of rubber elasticity is based on the fact that the unstrained rubber block is a statistically isotropic network of segments of chain molecules held together by randomly distributed junctions. More precisely this means that if the distances between neighboring junction points are represented by vectors expressing their magnitude and direction, the distribution exhibits a spherical symmetry, i.e., the probability of vectors of a given length is independent of their direction. It is assumed that on unidirectional elastic strain this spherical symmetry of the distribution changes to that of a rotational

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ellipsoid (on extension the ellipsoid is of an oblong, on compression of a flat character)[3]. Furthermore assuming that the lengths of the vectors are distributed according to a Gaussian probability function, the well known statistical expression of rubber elasticity is easily obtained. The theory supposes that all volume elements which have a similar shape as the whole of the body undergo a deformation proportional to that of the whole. This assumption appears to be a satisfactory approximation in the case of the most commonly examined simple extension, in the case of compression, however, it would be acceptable only if the faces of the rubber block in contact with the pressing surfaces were permitted to glide freely thereon (in this case, e.g., a compressed cylinder would presumably remain cylindrical). In practice, however, only completely fixed surfaces are dealt with, which naturally remain unstrained and, as indicated above, this is the effect which must be compensated by an increase of the free surface. The network structure of the rubber, however, makes it impossible that the surface should be increased by new chains coming to the surface from the interior of the block, and consequently the original surface network must get into a stressed state. The shape of the surface so formed is obviously determined by the condition that the stress in the surface network should be the same in all directions (along the surface), for the network should give way to any resulting stress pointing to some distinct direction. The surface network is forced apart in this way by the lateral elongation of the interior of the block. This means that there must be an unambiguous relation between the shear stress in the interior of the block and the surface stress on the other part.

From this relation between the stresses arising on compression, it should be possible in principle to calculate not only the shape adopted on deformation of the blocks, but the relation between the pressure acting on the fixed surfaces and the change in height, i.e., the stress-strain function as well. Actually, however, the problem could not be solved in this fashion as yet. Instead, in the subsequent treatment we have chosen an approximate procedure by introducing a correction term beside the term expressing the elastic resistance of the main body of the block which latter term may be taken as identical with the usual statistical expression. The new correction term contains the stress surplus in the surface coming from the lateral strains, as determined empirically by the measured surface increase.

The relation between stress p (the perpendicular force acting upon the unit of bound surface area) and deformation λ (the ratio of the block's actual and original heights) may be derived from the expression of the work of deformation, the differential of this per unit volume of the block being:

$$dW = pd\lambda \tag{1}$$

According to our assumptions outlined above the work dW is composed of two parts. One of these, the work done against the elastic resistance of the whole of the block, can be expressed by:

$$d_1W = Gf(\lambda)d\lambda \tag{2}$$

where according to the statistical theory of rubber elasticity

$$f(\lambda) = \lambda - \frac{1}{\lambda^2} \tag{3}$$

and G is the shear modulus of the rubber specimen.

In order to find an explicit expression for the part of the whole work associated with the increase of the free surface area let it be assumed that the stress σ striving to bring the surface back to its original dimensions can be put in the form:

$$\sigma = Hg(\alpha) \tag{4}$$

where H is some characteristic constant and g some function of the relative surface α awaiting explicit expression. At the moment it can be stated only that this function must disappear when $\alpha = 1$ and must be otherwise a monotonous increasing function of α. The work done when increasing the whole of the free surface F by a relative increment $d\alpha$ follows from (4):

$$dL = FHg(\alpha)\, d\alpha \tag{5}$$

As the total work in (1) has been referred to the unit volume of the block, the surface work (5) must be expressed in the same way, giving:

$$d_2W = \frac{dL}{V} = \frac{F}{V} Hg(\alpha)\, d\alpha \tag{6}$$

where V is the volume of the block.

The experimental fact that the stress-strain curves of blocks having the same shape are independent of their absolute dimensions justifies the assumption that for a given shape α must be an unambiguous function of λ only, that is:

$$d\alpha = \frac{d\alpha}{d\lambda}\, d\lambda \tag{7}$$

On the assumption that:

$$dW = d_1W + d_2W \tag{8}$$

the stress p can be expressed from (1):

$$p = \frac{dW}{d\lambda} = Gf(\lambda) + \frac{F}{V} Hg(\alpha) \frac{d\alpha}{d\lambda} \tag{9}$$

Here the right hand side is, apart from the constant characteristic of the rubber substance, a function of the deformation, but its second term is a function of the shape of the rubber block as well. Hence (9) is the sought equation of the stress-strain curve, which may be, however, of use only if explicit forms could be found for the functions $Hg(\alpha)$ and $\alpha = \alpha(\lambda)$.

To determine the form of the first of the above functions it should be considered that all intermediate layers of the rubber block subjected to compression undergo shear deformation parallel to the surfaces to which the pressure is applied, this shear leading to a bulging of the free lateral faces. Hence there must be an intimate relationship between the shear and the tension of the surface. This relationship may be demonstrated on the following model. Let us consider a prism with edges a, b and c (Figure 1) which undergoes an elastic shear deformation by the force K acting in the way and at the place shown in the figure. For not too large values of the angle of deformation:

$$K = Gbc \operatorname{tg} \varphi = Gbc \frac{h}{a} \tag{10}$$

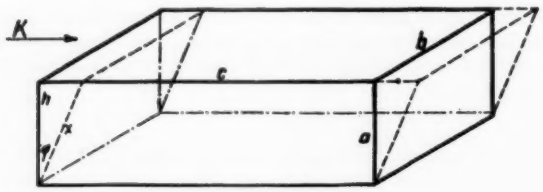

FIGURE 1.

where G is the shear modulus. It is obvious, however, that the front of the prism undergoes a simultaneous increase from ab to xb, and that the surface tension induced thereby is given by the part of the component of force K lying in the plane xb and perpendicular to the edge b, referred to unit length of edge b, that is:

$$\sigma = \frac{K}{b} \cdot \sin \varphi = \frac{K}{b} \frac{h}{x} \tag{11}$$

When expressing K from (10) and making use of the expression (4) of σ, and considering that the free surface of the prism is $F = ab$ and its volume $V = abc$ it follows that:

$$\frac{F}{V} Hg(\alpha) = G \frac{h^2}{ax} \tag{12}$$

It is also apparent from the figure that the relative increase of the surface is

$$\alpha = \frac{xb}{ab} = \frac{x}{a} \tag{13}$$

furthermore $h^2 = x^2 - a^2$. With these equations (12) may be further transformed:

$$\frac{F}{V} Hg(\alpha) = G \frac{x^2 - a^2}{ax} = G \left[\frac{x}{a} - \frac{a}{x} \right] = G \left[\alpha - \frac{1}{\alpha} \right] \tag{14}$$

As (14) no longer contains the dimension characteristic of the prism in question and, moreover, any rubber block can be built of rectangular prisms to any desired degree of accuracy, it seems a safe assumption that this relationship is of general applicability. As a result of the foregoing (9) may be put in the form:

$$p = G \left[\left(\lambda - \frac{1}{\lambda^2} \right) + \left(\alpha - \frac{1}{\alpha} \right) \frac{d\alpha}{d\lambda} \right] \tag{15}$$

The function $\alpha(\lambda)$, which is still unknown, cannot be given a general form since it depends on the shape of the rubber block. At present our experiments and calculations comprise only rubber blocks having either a cylindrical or square prismatic form.

I. CYLINDRICAL BLOCKS

Let the radius of the cylinder be r and its height m. On compression this height decreases to $m\lambda$. Figure 2a shows a photograph of a cylinder where

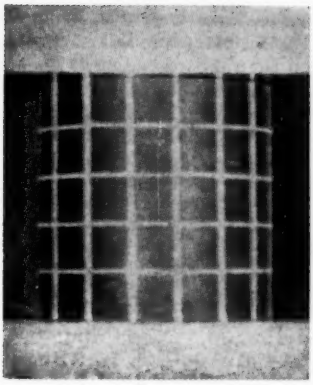

FIGURE 2a

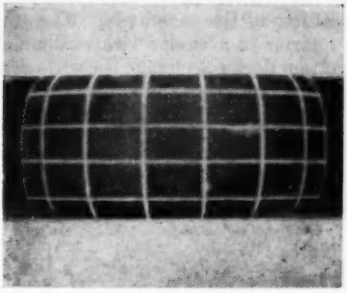

FIGURE 2b

$m = 2r$. In order to have a better picture of the deformations occurring on compression, a network was painted on the mantel of the cylinder. Figure 2b shows the photograph of the same cylinder under compression. It is seen that the middle part (about $\frac{3}{5}$th) of the compressed cylinder remains approximately cylindrical, though the generatrices show even here a slight barrel-like bulge. At the lower and upper parts, however, the generatrices join the pressing surfaces with a strong curvature, and the cylinder leans against those surfaces in close contact with them at a greater width than in its original state. No simple function could be found to describe the deformation of the generatrices precisely, and therefore an approximation of the actual deformation has to be used which appears to be satisfactory for the computation of the surface-increase.

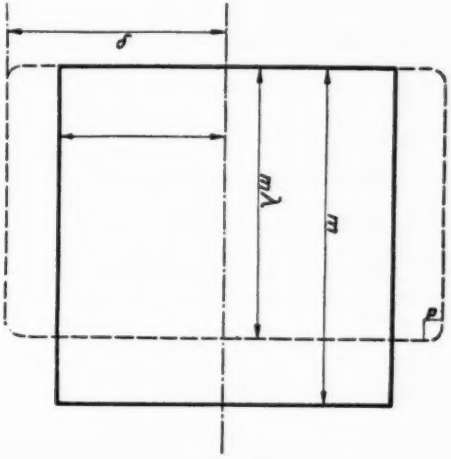

FIGURE 3.

The slight barrel-like bulge in the middle may be thought of being eliminated by means of some squeezing ring. By this procedure this part is transformed to a real cylinder of radius ρ. Then the rubber evading this squeeze must flow into the lower and upper parts, increasing simultaneously the joining curvatures of the generatrix. The curve obtained in this way is taken to be the quarter of a circle, with radius d. Visibly this additional imaginary deformation does not change the surface area by any considerable amount. This simplified picture of the actual deformation is shown in Figure 3.

The volume of the cylinder when unloaded is:

$$V = \pi r^2 m \tag{16}$$

whereas that of the deformed body as shown in Figure 3 is:

$$V = \pi\rho^2 m\lambda - \pi\left[(4 - \pi)(\rho - d)\, d^2 + \frac{2d^3}{3}\right] \tag{17}$$

As d is always relatively small, the second term, containing this quantity only in higher powers, is a practically negligible correction. Since the volume of the rubber block remains unchanged on compression, on comparison of the right hand sides of (16) and (17)

$$r^2 \approx \rho^2\lambda \tag{18}$$

is obtained, or:

$$\rho = \frac{r}{\sqrt{\lambda}} \tag{19}$$

. The next task is to compute the increase of the free surface. The free surface of the original cylinder is made up only of its mantle, that is

$$F(1) = 2\pi r m \tag{20}$$

The free surface of the deformed body as shown in Figure 3, however, is given by (the part of the original cylinder's mantle now in close contact with the pressing surfaces is taken as "free" surface as well):

$$F(\lambda) = 2\pi\rho m\lambda + 2\pi(\rho^2 - r^2) - 2\pi[\rho d(4 - \pi) + d^2(\pi - 3)] \tag{21}$$

Part of the last term, due to the rounding off of the edges, contains now the first power of d and this cannot be neglected (the second degree term in d, however, may be neglected in this case too).

Observations made on cylinders compressed to various extents led to the assumption that the radius of the curvature d can be taken proportional to the increase of the radius of the cylinder's mantle, that is

$$d = k(\rho - r) \tag{22}$$

The increase of the free surface is evidently:

$$\alpha(\lambda) = \frac{F(\lambda)}{F(1)} \tag{23}$$

When substituting into Expression (21) of $F(\lambda)$ the value (22) of d and that of ρ according to (19), and neglecting the second degree term with respect to d,

$$\alpha(\lambda) = \sqrt{\lambda} + \frac{r}{m}\left(\frac{1}{\lambda} - 1\right) - k\frac{r}{m}(4 - \pi)\left(\frac{1}{\lambda} - \frac{1}{\sqrt{\lambda}}\right) \tag{24}$$

is obtained.

The quotient r/m in this equation is a value characteristic of the shape of the cylinder, giving the ratio of free and fixed surfaces, which could also be called "stockiness"-index. This index is generally used to characterize the shape of rubber springs. From (24) it follows that the relative surface-increase is a function not only of the relative compression λ but of the shape as well, a fact emphasized by writing:

$$\alpha(\lambda, \delta) = \sqrt{\lambda} + \delta\left(\frac{1}{\lambda} - 1\right) - k\delta(4 - \pi)\left(\frac{1}{\lambda} - \frac{1}{\sqrt{\lambda}}\right) \tag{25}$$

where $\delta = r/m$ is the above mentioned index of stockiness. The differential quotient occurring in the basic equation (15) is obtained by differentiating (25):

$$\frac{\partial\alpha(\lambda, \delta)}{\partial\lambda} = \frac{1}{2\sqrt{\lambda}} - \frac{\delta}{\lambda^2} + k\delta(4 - \pi)\left(\frac{1}{\lambda^2} - \frac{1}{2\lambda\sqrt{\lambda}}\right) \tag{26}$$

It should be noted that with the values of k to be determined in the following (0.57 with the cylindrical body, 0.46 with the quadratic prism) in the case of slenderer bodies (with cylinders $\alpha < 0.662$, with prisms $\alpha < 0.623$) the values of α according to (25) show a very little decrease at the start alongside with λ. The minimum value of α is 0.987 and 0.992, respectively, when $\delta = 0.5$. On greater compressions, however, α increases rather rapidly even in this case. This behavior of the function does not mean that with slenderer bodies the surface should actually decrease at the start of the deformation, but only that the idealized picture of the deformation as shown in Figure 3 is not a satisfactory approximation in this range. Hence with the bodies included in our tables with the value $\delta = 0.5$ we chose to use the value $\alpha = 1$ in the range where according to (25) $\alpha < 1$ would have been obtained. This is equivalent to neglecting the correction term in Equation (15); i.e., with blocks of such a shape (not usual in spring technique) we simply apply the usual statistical expression of rubber elasticity in the range of small compressions. The results so obtained are entirely satisfactory.

Substituting the expressions thus obtained into (15), this equation becomes suitable for the computation of the stress-strain curves, assuming that the shear modulus G and the numerical factor k are known. The latter is determined according to (22), the measurements made on the photographs 2a and 2b yielding:

$$r = 33.7 \text{ mm} \quad \rho = 40.8 \text{ mm} \quad \text{and} \quad d = 4.05 \text{ mm}$$

and hence:

$$k = \frac{d}{\rho - r} = 0.57$$

To test the validity of the expression obtained, rubber cylinders of different stockiness (but having equal bases of 1 cm^2) were made and their stress-strain curves determined in Höppler's consistometer at 25° C. The amount of strain was read ten minutes after the stress had been applied in order to eliminate the effect of a slight initial relaxation. As the base and upper faces hardly can be obtained strictly parallel in the process of vulcanization, the starting point of the stress-strain curve had to be established from the curve itself by extrapolation. The composition of the rubber compound used is as follows:

Rubber	100.0
Sulfur	2.8
Carbon black (soft)	20.0
Mercaptobenzothiazole	0.8
Antioxidant	0.3
Stearic acid	3.7
Pine tar	2.2
ZnO	5.0

The value of the shear modulus G was found to be 9 kg/cm^2 from the measurements made on a rubber clyinder with index $\delta = \frac{1}{3}$.

The experimental results are shown in Figure 4. There the solid lines represent the curves calculated by (15) for the corresponding values of δ indicated in the figure, using the values $G = 9$ kg/cm^2 and $k = 0.57$. The marks represent measured data. It can be seen that the calculation yields values in perfect agreement with the experimental data within the limits of error of the latter. It should be noted that these limits are, especially in case of small deformations, relatively great.

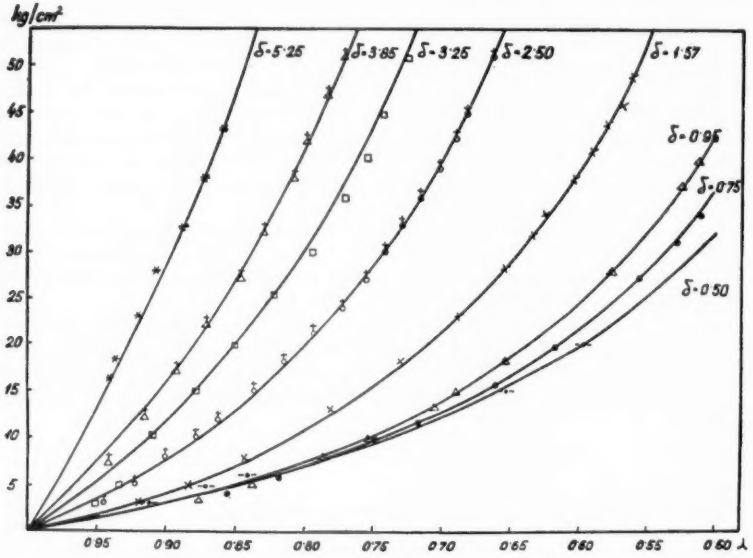

FIGURE 4.

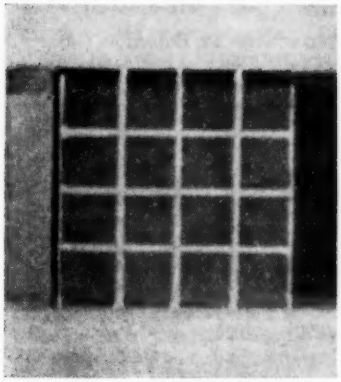

FIGURE 5a

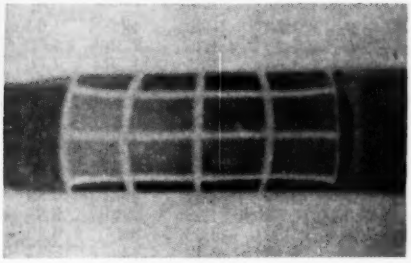

FIGURE 5b

II. QUADRATIC PRISMS

Figures 5a and 5b show photographs of a rubber cube in unloaded and loaded state, respectively. It can be seen therefrom that in this case too, considerable parts of the free edges of the cube remain straight, that is the edges of the cube undergo a deformation similar to that of the generatrices of the cylinder. Hence the actual deformation can be approached in the same way, that is Figure 3 can be regarded as the idealized section of the deformed quadratic prism as well, the only difference being that the diameter $2r$ of the cylinder should be replaced by the edge of the base of the prism. The computation of the volume and the surface made by this substitution yields the same result already obtained for the cylinder in Part I, i.e., Equations (25) and (26) retain their validity even in this case. The stockiness index is, in the case of quadratic prisms, also given by the ratio of the fixed and free surfaces, that is:

$$\delta = \frac{a}{2m} \tag{27}$$

The value of the coefficient k, however, is somewhat smaller in the case of quadratic prisms than in the case of cylinders. From measurements made on the photographs 5a and 5b $a = 86.4$ mm, $a' = 115.5$ mm and $2d = 13.2$ mm. Hence:

$$k = \frac{13.2}{115.5 - 86.4} = 0.46$$

No detailed measurements were made by us with quadratic prisms, the measurements of Jenkins[4] being available to test the validity of the equations deduced in this paper. Jenkins published the results of his measurements on quadratic prisms of varying heights in a graph containing curves which show the stress p relative to that of a cube ($\delta = 0.5$) of the same material as a function of 2δ, at different values of λ. Let this proportional number be η, that is:

$$\eta = \frac{p(\lambda, \delta)}{p(\lambda, \frac{1}{2})} \tag{28}$$

TABLE I

COMPARISON OF THE RELATIVE STRESSES CALCULATED BY EQUATION (15) AND THE VALUES GIVEN BY JENKINS

2δ	$\lambda = 0.95$		$\lambda = 0.80$		$\lambda = 0.60$		$\lambda = 0.50$	
	$\eta_{calc.}$	$\eta_{lit.}$	$\eta_{calc.}$	$\eta_{lit.}$	$\eta_{calc.}$	$\eta_{lit.}$	$\eta_{calc.}$	$\eta_{lit.}$
1.0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2.5	1.20	1.35	1.36	1.50	1.64	1.70	1.85	2.02
3.0	1.38	1.55	1.59	1.76	2.03	2.06	2.33	2.51
3.5	1.62	1.78	1.91	2.01	2.49	2.53	2.90	3.13
4.0	1.91	2.04	2.28	2.30	3.04	3.10	3.53	3.88
4.5	2.27	2.31	2.72	2.67	3.65	3.79	4.30	4.70
5.0	2.60	2.66	3.06	3.10	4.34	4.57	5.13	5.61
5.5	3.16	3.07	3.73	3.67	5.09	5.39	6.02	6.55
6.0	3.64	3.59	4.34	4.36	5.88	6.32	7.02	7.61
6.5	4.22	4.24	4.99	4.88	6.77	6.90		
7.0	4.83	4.98	5.69	5.85	7.72	8.20		
7.5	5.52	5.68	6.44	6.50				
8.0	6.19	6.42	7.25	7.47				
8.5	6.96	7.16	7.99	8.16				
9.0	7.76	7.84	8.95	9.14				

It is evident that such presentation of the results eliminates the shear modulus and, consequently, applies equally to any rubber specimen.

In Table I the values of η read from the diagram of Jenkins at $\lambda = 0.95$, 0.80, 0.60 and 0.50 are compared with those computed by (15) assuming that $k = 0.46$. Table II shows the values of the relative increase of the free surface at the same points as given in Table I. The figures in Table I show that the differences between values calculated by (15) and Jenkins' experimental data remain below 10 per cent even in case of a threefold increase of the surface. With smaller deformations the agreement is considered to be within the limits of experimental error (including the errors of reading Jenkins' graph).

It is mentioned in the paper of Jenkins referred to that his measurements were extended also to cylindrical bodies. Without giving detailed data, it is stated only that stresses measured on cylinders are in general smaller by a factor of 0.9 than those obtained with quadratic prisms with identical values of δ. In the equation deduced here the difference between the two different bodies appears only in the value of the factor k (0.57 with the cylinder and 0.46

TABLE II

THE SURFACE-INCREASE OF QUADRATIC PRISMS BY EQUATION (25)

2δ	$\lambda = 0.95$	$\lambda = 0.80$	$\lambda = 0.60$	$\lambda = 0.50$
1.0	1.000	1.000	1.035	1.090
2.5	1.028	1.142	1.425	1.665
3.0	1.038	1.191	1.555	1.856
3.5	1.049	1.241	1.685	2.048
4.0	1.059	1.290	1.815	2.239
4.5	1.070	1.340	1.945	2.431
5.0	1.080	1.389	2.075	2.622
5.5	1.091	1.439	2.205	2.814
6.0	1.101	1.488	2.335	3.005
6.5	1.112	1.538	2.465	
7.0	1.122	1.587	2.595	
7.5	1.133	1.637		
8.0	1.143	1.686		
8.5	1.154	1.726		
9.0	1.164	1.785		

with the quadratic prism). With these values of k the present equation yields for the ratio of stress arising in the two different bodies in the range of η comprised by Table I values varying between 0.88 and 0.94, hence there is a perfect agreement with the data of Jenkins in this respect as well.

SUMMARY

For the stress-strain relation of differently shaped rubber blocks submitted to compression, an equation of general applicability is deduced, starting from the idea that compression work must be done also against the tension arising through the increase of the free surface. In this equation the stress is not a function of the compression ratio only, but of the ratio of the fixed to the free surface as well. Besides the shear modulus of the block's substance, this equation involves a single empirical constant which changes only slightly with the shape of the block's cross section. The validity of the equation obtained was tested by measurements performed by the authors on cylinders as well as by data on quadratic prisms published in previous literature. The calculated values are in good agreement with the experimental data within the limits of experimental error.

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STRESS-STRAIN RELATIONS IN RUBBER BLOCKS UNDER COMPRESSION. II *

O. Dessewffy, G. Schay, and P. Ször

Central Research Laboratory of the Rubber Industry, Budapest, Hungary

In designing rubber springs subjected to compression it is essential to know the exact relationship between strain and stress. It would be a great facility to designers if formulas were available from which to calculate this relation for blocks of any given shape, based on some measurable physical property of the rubber quality alone. At present, neither the statistical theory of rubber elasticity nor its modification permit of such formulas to be deduced. The statistical theory enables us, of course, to compute stresses occurring within a limited range of homogeneous strains; this is, however, of little practical use, since rubber blocks are usually compressed under conditions which produce inhomogeneous strains.

In a previous paper (Communication I[1]) we dealt with that sole instance of practical importance in which the compressive stress is acting upon two parallel faces of the rubber block and these faces are fixed to contiguous rigid surfaces (metal fittings) so as to prevent their slipping. Surfaces so fixed remain unaltered when the block is set under compression, consequently only the free sides suffer deformation and this, according to experience, is always accompanied by an increase of the lateral surfaces, when shape and strain are those usual in practice. This experimentally verified fact has led to the deduction of a formula which expresses correctly the relationship of stress and strain in quadratic rubber prisms and cylindrical rubber blocks, provided compression takes place between parallel plates larger than the compressed surfaces. In this paper it is intended to ascertain the stress-strain relations in rectangular and annular rubber bodies by applying the same principles as were adopted in the case of quadratic prisms and cylindrical bodies, with a special view to facilitate the task of designers.

RECTANGULAR BLOCKS

Let the edges of the rectangular body before compression be a, b, m, and those of the rectangular body approaching the shape deformed by compression, a', b', m'. The volume of rubber being invariable to strain, we can write as a first approximation

$$abm = a'b'm' \tag{1}$$

By introducing the terms

$$\frac{a'}{a} = x; \quad \frac{b'}{b} = y; \quad \frac{m'}{m} = \lambda \tag{2}$$

* Reprinted from *Acta Chimica Academiae Scientiarum Hungaricae*, Vol. 7, pages 393–401, 1955.

the condition of constancy of volume may also be expressed as

$$xy\lambda = 1 \tag{3}$$

This is an approximation insofar as it disregards the rounding off of the edges upon compression. In reality the edges of brick-shaped blocks are rounded off when deformed wherefore, strictly, the volume a', b', m', ought to be diminished by an adequate correction. This correction is, however, small enough to be neglected without any serious error. To obtain the values of x and y, i.e., the relative changes of the edges of the base as an explicit function of strain, one more equation is required which refers to the increase in the area of the free surfaces of the block. The free surface of our parallelepipedon is made up of two parts:

$$F_{01} = 2am \quad \text{and} \quad F_{02} = 2bm \tag{4}$$

These surfaces are deformed by compression. Their values can be obtained from three surface portions as detailed in Communication I[1];

$$F_1 = 2\left[a'm\lambda + \left(\frac{a' + a}{2}\right)(b' - b) - da'(4 - \pi)\right] \tag{5}$$

$$F_2 = 2\left[b'm\lambda + \left(\frac{b' + b}{2}\right)(a' - a) - db'(4 - \pi)\right] \tag{6}$$

where d is the radius of curvature of the block's rounded off surface. Its value is directly proportional to the change in the block's linear dimensions:

$$d = k\left(\frac{b' - b}{2}\right) \quad \text{or} \quad d = k\left(\frac{a' - a}{2}\right) \tag{7}$$

With $b > a$ and

$$\frac{b}{a} = \rho_t, \quad \frac{a}{2m} = \delta_t \tag{8}$$

the relative changes (α_1, α_2) may be expressed as

$$\alpha_1 = x\lambda + \delta_t\rho_t(B - Ax + y) \tag{9}$$

$$\alpha_2 = y\lambda + \delta_t(B - Ay + x) \tag{10}$$

where

$$A = 1 - k(4 - \pi) \quad \text{and} \quad B = \frac{A}{\lambda} - 1 \tag{11}$$

Let it now be assumed that the relative expansions of the smaller and larger free surface portions of our parallelepipedon are identical, i.e.,

$$\alpha_1 = \alpha_2 = \alpha \tag{12}$$

The surface tension must have the same value at every point, as otherwise unidirectional stresses would occur, and the rubber specimen would yield in their direction. Hence, our above assumption implies the existence of an unequivocal relation between surface tension and surface expansion which must

be valid at every point of the surface. This assumption was implicit also in Equation (15) or Communication I[1].

It is now possible to obtain α as a function of λ by solving the simultaneous Equations (3) and (12) for the unknown x and y. The validity of Assumption (12) has been tested experimentally. Having measured the shorter and longer edges of the base of compressed parallelepipedal rubber blocks and thus ascertained the values of x and y, the relative surface expansions were calculated from Equations (9) and (10). Figure 1 shows these increases as functions of the strain ($\delta_t = 1.0$ $\rho_t = 1.5$). It will be seen that the values found for α_1 and α_2

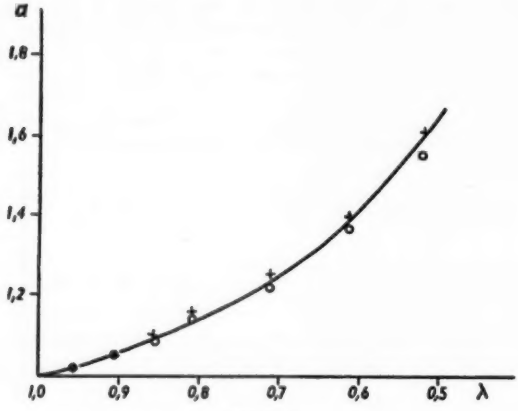

FIGURE 1.

agree within the experimental errors. The continuous curve represents the function $\alpha(\lambda)$ as calculated theoretically from Equation (12).

The value of $\frac{d\alpha}{d\lambda}$, required to calculate the stresses occurring on compression, may be obtained by differentiating either Equation (9) or (10). E.g., from (9):

$$\frac{d\alpha}{d\lambda} = x + \lambda \frac{dx}{d\lambda} + \delta_t \rho_t \left[\frac{dB}{d\lambda} - A \frac{dx}{d\lambda} + \frac{dy}{d\lambda} \right] \tag{13}$$

It can be seen that the values of both α and $\frac{d\alpha}{d\lambda}$ depend not only upon strain but also upon the shape parameters δ_t and ρ_t. While one such parameter sufficed to characterize cylindrical bodies and quadratic prisms, two are necessary to define the form of brick-shaped blocks. In our present calculations, the value of the proportionality factor k was taken as 0.46, i.e., the same as in the case of quadratic prisms.

To check the validity of the results deduced theoretically, brick-shaped rubber blocks with various characteristics δ_t and ρ_t were made. From measurements performed on cubes ($\delta_t = 0.5$; $\rho_t = 1$; $x = y$) made from the same rubber quality, the value of the shear modulus was determined to be 9 kg/cm^2. A compression machine with a maximum load of 5000 kg was used to compress

the rubber blocks. In order to eliminate the effect of relaxation, values of strain and stress were read 10 minutes after loading. The compressed surfaces underwent no tangential displacement with reference to the parallel plates since slipping was prevented by the use of somewhat rough pressing surfaces. The measured stresses were, within the limits of experimental error, in good agreement with calculated values. Figure 2 illustrates the stress-strain relations found in some rectangular rubber blocks, while the continuous curves represent the theoretical stress function.

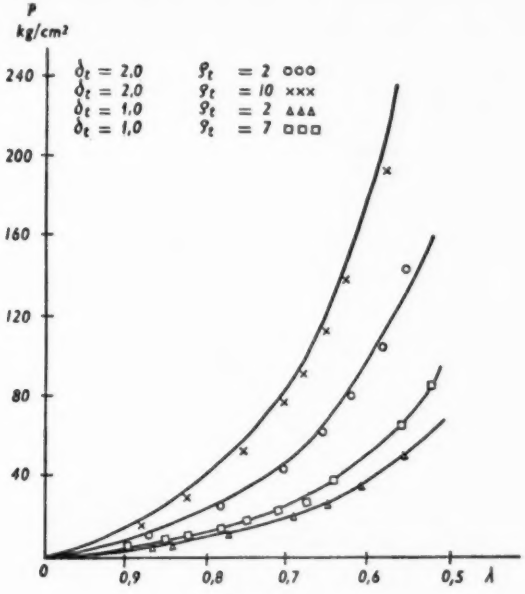

FIGURE 2.

Although our formulas have been confirmed by experiment we endeavored to find a simpler way to calculate theoretically the stress-strain relation in rectangular rubber blocks, since the above method, requiring as it does a great many numerical operations, seemed to be somewhat cumbersome for practical use.

The ratio of the fixed and free surfaces in brick-shaped bodies is

$$\delta = \frac{ab}{(a+b)m} \tag{14}$$

It was found that the p/G values for these bodies were, to an accuracy of $\pm 4\%$, in agreement with the values calculated for quadratic prisms, provided the above δ was substituted for the "index of stockiness" in Equation (25) of Communication I[1]. When designing rubber springs a certain variance in hardness (modulus) must be taken account of. Therefore, in the design of brick-shaped

rubber blocks the stress-strain relation valid for quadratic rubber prisms can be applied with satisfactory results. Owing to its simplicity, this procedure is more suitable for practical purposes. It must, of course, be borne in mind that the "index of stockiness" (δ) in Equation (25) of Communication I means the quotient of the fixed and free surfaces if applied to brick-shaped bodies.

ANNULAR BODIES

Attempts to ascertain the stresses in these bodies by calculating the approximate relative expansions of the free surfaces with the above method will not yield correct results. Employing the notations R and r for the outer and inner

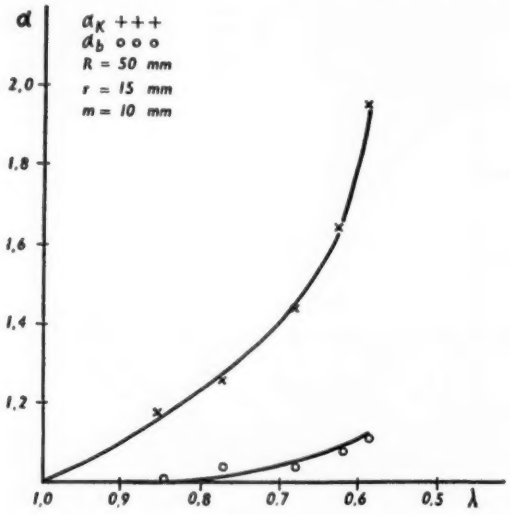

FIGURE 3.

radius and m for the height of the annulus before, and R', r' and m' after deformation, and introducing the variables

$$\frac{R'}{R} = x, \quad \frac{r'}{r} = y, \quad \frac{m'}{m} = \lambda \tag{15}$$

the postulate of constant volume can be expressed as

$$\frac{R^2 - r^2}{\lambda} = R^2x^2 - r^2y^2, \tag{16}$$

the rounding-off of the generatrices being disregarded. One more relation is, however, required to obtain the values of x, y, α and $\frac{d\alpha}{d\lambda}$. If, in analogy to parallelepipedons, it is assumed that the relative change in the area of the outer

free surface is identical with that of the inner one, the calculated stresses will be less than those measured. It was proved by direct experiments also that the relative expansion of the outer lateral surface of annular bodies differs from that of the inner one. Annular blocks were compressed applying a top pressure plate pierced in the middle, and after deformation molten paraffin was cast in the empty inner circle of the annuli. Having measured the circumference of the solidified paraffin molds and the outer free surface of the annuli, the expansion of the inner surface was invariably found to be less than that of the outer one. Figure 3 shows, for the case of one annular rubber block, the relative expansions of these two kinds of free surfaces as functions of strain. The outer surface can be seen to have expanded considerably more than the inner one.

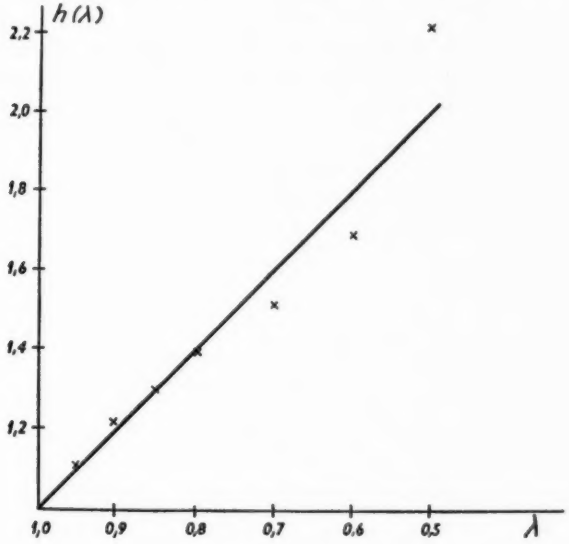

FIGURE 4.

An exact mathematical description of these surface changes is further complicated by the fact that, when the strain exceeds a certain limit, the inner free surface will wrinkle or touch.

Having ascertained from experiments that stresses occurring on compression of brick-shaped blocks can be calculated with sufficient accuracy by substituting the quotient of the fixed and free surfaces in the simpler formulas obtained for quadratic prisms, we tried a similar method in the case of annular bodies. In Equation (25) of Communication I referring to cylindrical bodies, we substituted the ratio of fixed and free surfaces of annular bodies for the "index of stockiness", but again found that the calculated stresses were considerably less than the measured ones. It is therefore not possible to calculate the stresses occurring on compression in annular bodies from our above relation, by accounting for the shape of the rubber block by the ratios of fixed to free surfaces.

Thereafter we attempted to establish an empirical relationship between

stress and strain in annular bodies subjected to compression. The ratio of fixed and free surfaces is

$$\delta = \frac{R - r}{m} \tag{17}$$

The same as with rectangular bodies, two parameters are required to characterize the shape of such blocks precisely, but measurements showed that, up to about 25% deformation and within ±5%, stresses occurring on compression depend upon δ only; in other words, stresses in the range of slight strains are unequivocally defined by the ratio of width to height also in the case of annular

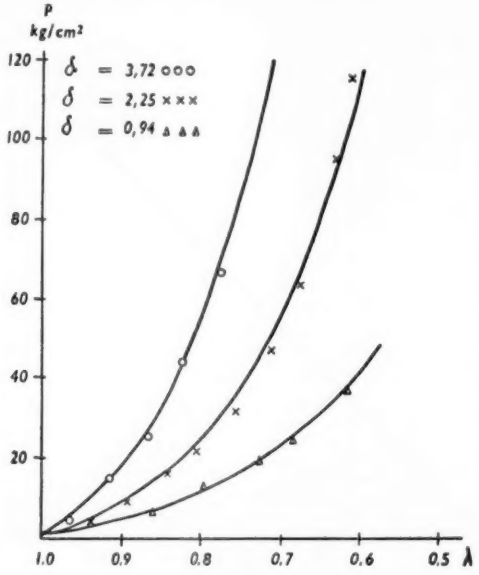

FIGURE 5.

bodies. Comparing the measured stresses with the theoretical values obtained from Equations (15) and (25) of Communication I for cylindrical bodies having identical characteristic δ-values, we determined, at various strains, the ratios of these two kinds of stresses. Their mean values expressed as functions of the strain are shown in Figure 4. The dispersion with reference to δ of the ratios pertaining to identical strains is less than 10% in the range of strains up to 20%. In the region of slight strains their mean values lie approximately on a straight line. Since strains over 20% are of no practical importance in the design of rubber blocks to be subjected to compression, in this region the dependence of these ratios upon λ can be taken as approximately linear. Stresses occurring on compression of annular bodies may therefore be calculated from the formula

$$p = G\left[\left(\lambda - \frac{1}{\lambda^2}\right) + \left(\alpha - \frac{1}{\alpha}\right)\frac{d\alpha}{d\lambda}\right] h(\lambda), \tag{18}$$

where the ratio $h(\lambda)$ independent of δ in the range of strains up to 20%, its value being

$$h(\lambda) = 3 - 2\lambda \tag{19}$$

The value of α can again be obtained from Equation (25) of Communication I[1] which refers to cylindrical bodies. As an example, Figure 5 shows the stress-strain relation for 3 annular rubber blocks. The continuous curves represent the functions $p(\lambda, \alpha)$ as derived from Equation (18).

SUMMARY

The formula $p = G\left[\left(\lambda - \frac{1}{\lambda^2}\right) + \left(\alpha - \frac{1}{\alpha}\right)\frac{d\alpha}{d\lambda}\right]$, deduced previously, has been applied to rectangular and annular rubber blocks. Measurements have shown, that, while this equation remains valid for brick-shaped bodies, to annular bodies it can be applied up to about 20% deformation only if the right side is multiplied by the function $h(\lambda) = 3 - 2\lambda$.

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MEASUREMENT OF THE ISOTHERMAL VOLUME DILATION ACCOMPANYING THE UNILATERAL EXTENSION OF RUBBER *

FRED G. HEWITT AND ROBERT L. ANTHONY

DEPARTMENT OF PHYSICS, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA

INTRODUCTION

As is well known, the differential Poisson's ratio for a soft gum rubber is very nearly 0.5. Hence the change in volume accompanying the unilateral extension of such a rubber is very small. In spite of its small magnitude, this volume change is believed to be responsible for the major part of the internal energy component (strictly speaking, the enthalpy component) of the equilibrium rubber stress-strain curve in the low extension region[1,2]. Thus the determination of this volume change is important to a proper understanding of the thermoelastic behavior of rubbers.

Holt and McPherson[3] were among the first to attempt a measurement of this volume increase for a soft gum rubber. For extensions ranging from 0 to 200%, they were unable to detect any change in volume. Their work did serve, however, to place an upper limit on the possible magnitude of this volume increase, namely that it had to be less than 0.2%, which figure represented their experimental uncertainty. The first successful measurements reported in the literature appear to be those of Gee, Stern, and Treloar[2]. Using natural rubber ring specimens cured with di-tertiary-butyl-peroxide (DTBP), these workers measured the increase in volume for samples having chain molecular weights of 4900 and 9500. Measurements were confined to extensions lying in the approximate range of 40 to 110%. The volume increase observed ranged from about 0.006% to 0.02%, the largest value being observed for the sample of 4900 chain molecular weight at an extension of 110%. The work to be described was undertaken mainly for the purpose of extending the results of Gee, Stern, and Treloar to the region of lower strains.

EXPERIMENTAL

The rubber specimens used in this work were molded rings of rectangular cross section, having an inside diameter of 3.72 cm, an outside diameter of 5.05 cm, and a height of 1 cm. They were made from pale crepe natural rubber cured with di-tertiary-butyl-peroxide, 3 to 4 cc of DTBP per 100 g of raw rubber being added directly to the rubber on a mixing mill. The curing time for all samples was 6 hr at 280° F. The cured samples were quite transparent, and the presence of bubbles or foreign matter in the samples was easily detected. Only specimens free of visible defects were employed in the volume dilation studies. Extension of the rubber rings was carried out under water by rolling the rings down an aluminum cone on to light aluminum rings. Considerable

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care was exercised to ensure thorough wetting of the specimens and the elimination of air bubbles. Since the rubber ring specimens were quite thick, the extension varied considerably from the inside to the outside of the rings. The mean extensions employed in this work are volume average values. (In this connection it may be noted that an uncertainty of several per cent in the extension is of no great consequence in the present work.) Aluminum rings of three different diameters were employed, leading to mean extensions of 14, 33, and 51%. The four rubber specimens used in this work had chain molecular weights M_c = 5500, 5100, 4400, and 3000, with an uncertainty of approximately 10% in each value of M_c. The M_c values were determined by swelling in benzene and using Flory's formula[4]. A rough comparison was also made with the tabulated values of M_c vs swelling ratio given by Farmer and Moore[5]. The density of each rubber specimen, and also that of the milled raw rubber, was 0.910 g/cm^3 at 26° C.

The volume increase accompanying the isothermal extension of the rubber specimens was measured by hydrostatic weighing, using a sensitive torsion balance. Figure 1 is a schematic diagram of the torsion balance arrangement.

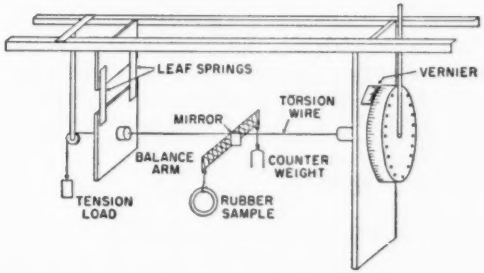

FIG. 1.—Schematic diagram showing torsion balance arrangement.

In order to eliminate the troublesome effects of surface tension at the water-air interface, the balance was designed for complete immersion in the water bath. The torsion wire was a 3-mil tungsten wire, about 30 cm long, and was nickel plated to reduce corrosion. The ends of the torsion wire were welded to small pieces of nickel sheet and mounted in plastic chucks. The balance arm was a 4-in. welded truss of 10- and 20-mil nickel wire, and carried a small front surface rhodium mirror. The balance arm was welded to the torsion wire near its midpoint. The plate holding the left chuck was hinged, being suspended from the overhead support by means of thin leaf springs of nickel. Proper tension in the torsion wire was maintained by a weight suspended from a rayon cord running over a bearing and attached to the hinged plate. The right chuck was mounted in a Teflon bearing and attached to a large brass dial graduated with 720 divisions around its circumference. A 10 division vernier served to indicate the dial position with good precision. A lamp and scale, located outside the bath and approximately 3 m in front of the mirror, was used as a null detection device. In making the volume dilation measurements, readings were taken to the nearest ½ degree division of the dial, the vernier being employed only during the calibration of the balance. The sensitivity of the balance was about 40 micrograms per ½ degree dial division.

The bath temperature for all measurements was 29.5° C. During a given series of measurements, the temperature was held constant to within ±0.005° C as determined with a Beckmann differential thermometer. The stirrer was shut off shortly before each reading was taken. In addition to this precaution, it was found necessary to introduce considerable baffling into the bath, in the vicinity of the balance arm, in order to supress the effects of slow, persistent eddy currents.

For the volume dilation studies an appropriate aluminum ring and the unextended rubber specimen were suspended from one side of the balance arm and counterbalanced. The rubber specimen was then extended, as previously described, and the change in buoyant force was determined from the angular rotation of the brass dial required to restore the null reading. A time of ap-

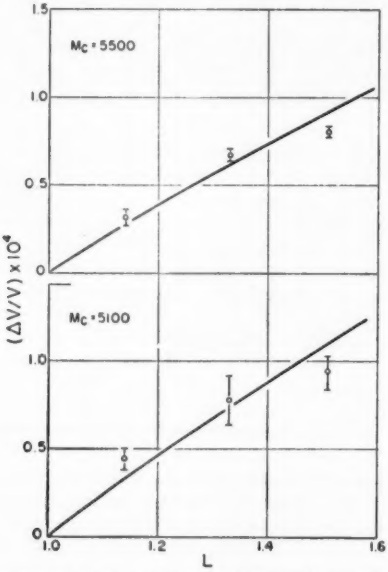

FIG. 2.—Fractional increase in volume, $\Delta V/V$, vs. relative length, L, for samples of chain molecular weight M_c =5500 and 5100; circles denote averages of experimental determinations; solid curves are theoretical curves based on Gee's expression.

proximately 15 min was allowed for the attainment of thermal equilibrium after changing the sample extension. The rubber samples were observed to absorb water at a constant rate of about 0.002 g/hr, resulting in a steady change in the underwater weight of the samples. This was taken into account in the measurements by taking readings regularly at 20-min intervals for five complete cycles of the stretched and unstretched condition of the sample. The nine successive differences were then averaged to provide a single determination of the fractional volume increase. A new extension was then employed and the process repeated.

RESULTS

Figure 2 shows the fractional increase in volume plotted as a function of the relative length (ratio of extended to unextended length), for rubber samples

having chain molecular weights of 5500 and 5100. The circles represent the averages of two individual determinations at each mean extension, each determination consisting of nine volume differences. The flags denote the spread of the individual determinations about the average value. The solid curves are theoretical curves based on Gee's[6] expression for the increase in volume as a function of extension. This expression may be written in the form

$$\frac{\Delta V}{V} = \frac{1}{3B}\int_1^L L\left(\frac{\partial F}{\partial L}\right)_{P,T} dL \tag{1}$$

where B is the bulk modulus of the rubber, P is the pressure of the surrounding fluid ($\sim$ 1 atmos), and T is the absolute temperature. $\Delta V/V$ is the fractional increase in volume, F is the stretching force divided by the cross sectional area of the unstrained sample, and L is the ratio of the extended to the unextended length of the sample. The definitions used for F and L are equivalent to normalizing the dimensions of the unstrained sample to those of a 1-cm cube. Since the shape of our samples was not conducive to the taking of good stress-strain curves, and since the statistical theory expression,

$$F = KT\,[L - 1/L^2] \tag{2}$$

describes the rubber stress-strain curve fairly well at low extensions and at constant temperature, we have employed Equation (2) to evaluate the derivative under the integral of Equation (1). Integration then yields

$$\frac{\Delta V}{V} = \frac{KT}{3B}\left[\frac{(L^2 - 1)}{2} + \frac{2\,(L - 1)}{L}\right] \tag{3}$$

as a final expression for the fractional increase in volume. The parameter K appearing in Equations (2) and (3) is related to the chain molecular weight M_c, the density ρ of the rubber, and the gas constant R by the relation $K = \gamma\rho R/M_c$. The precise value of the numerical factor γ is not known. It depends upon the particular version of the statistical theory employed, and also upon the detailed structure of the rubber network. A comprehensive discussion of this point is given by James and Guth[7]. Since γ appears to lie in the approximate range $\frac{1}{2}$ to 2, we have arbitrarily assumed it to be unity later in this work. The value of B employed by Gee, Stern, and Treloar[2], namely 1.9×10^{10} dynes/cm^2, was used in the present work. Equation (3) was fitted to the experimental points by adjusting the parameter K so as to make the average deviation equal to zero. This gave the theoretical curves shown in Figure 2.

Figure 3 shows the experimental results and their representation by the theoretical curve for samples having chain molecular weights of 4400 and 3000. In the case of the 4400 chain molecular weight sample, the spread in the experimental values of $\Delta V/V$ was rather large at the mean extensions of 33 and 51% and three separate determinations of the fractional volume increase were made at each of these extensions. Comparison of Figures 2 and 3 shows that for a given extension the fractional change in volume increases steadily with decreasing chain molecular weight. In other words, as M_c decreases the rubber tends to resemble more and more nearly a normal elastic solid.

The theoretical curves employed to describe the volume dilation were compared with similar curves given by Gee, Stern, and Treloar[2]. This comparison is shown in Figure 4, the dashed curves being those of Gee, Stern, and Treloar,

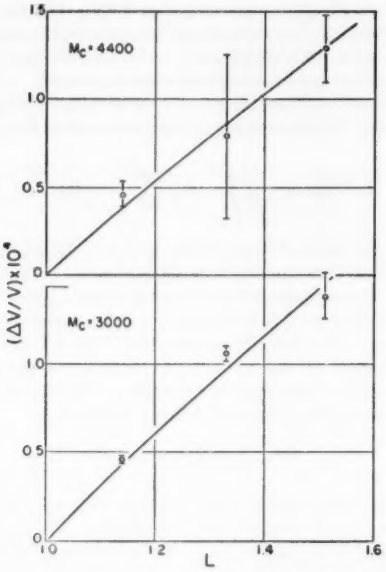

FIG. 3.—Fractional increase in volume, $\Delta V/V$, vs. relative length, L, for samples of chain molecular weight M_c = 4400 and 3000; circles denote averages of experimental determinations; solid curves are theoretical curves based on Gee's expression.

the solid curves referring to the present work. The agreement appears to be satisfactory, the curves for chain molecular weights of 5100 and 4900 even falling almost on top of each other. In view of the rather large uncertainty (about 10%) in our values of M_c, the near coincidence of the 5100 and 4900 chain molecular weight curves is somewhat fortuitous.

The process of fitting the theoretical curves to the experimental points by adjusting the parameter K constituted a determination of Young's modulus,

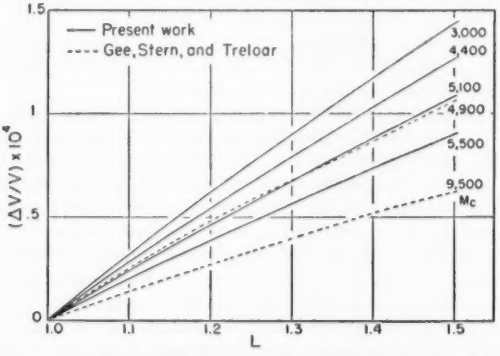

FIG. 4.—Comparison of theoretical curves with those of Gee, Stern, and Treloar.

since, according to the statistical theories of rubber elasticity, K is equal to $E/(3T)$, where E is Young's modulus evaluated at $L = 1$, and T is the absolute temperature[5]. As a check on the experimental work, and also on the theory employed, it was deemed worthwhile to attempt evaluations of E by two additional methods. Accordingly, after completing the volume dilation studies the rubber ring specimens were cut open and crude stress-strain curves were run. Young's modulus was then evaluated for each sample from the slope of the stress-strain curve at $L \simeq 1$. Finally, a third determination of E is provided by the relation $E = 3\gamma\rho RT/M_c$. Table I gives a comparison of the values of

TABLE I

E IN KG/CM^2

Method	Chain molecular weight, M_c 5500	5100	4400	3000
Fitting of theoretical curves	12	15	17	20
From stress-strain curves	13	14	16	19
$E = 3\gamma\rho RT/M_c$, $\gamma = 1$	13	14	16	23

E determined by the above three methods for the four different samples. With one exception the agreement is quite satisfactory. The high value of E as determined by the third method for the sample of 3000 chain molecular weight appears to indicate that the value of M_c used for this sample is too small.

SUMMARY

The fractional increase in volume accompanying the isothermal extension of soft gum rubber was measured for four rubber samples at mean extensions of 14, 33, and 51%. The chain molecular weights M_c of the four samples were 5500, 5100, 4400, and 3000, with an estimated uncertainty of about 10% in each value of M_c. The observed fractional increase in volume ranged from 3.2×10^{-5} to 14×10^{-5}, the latter value being observed for the sample of lowest chain molecular weight and at the extension of 51%. The experimental results for each sample have been represented by theoretical curves based on Gee's expression for the fractional increase in volume as a function of the sample extension. The theoretical curves exhibit good agreement with those of Gee, Stern, and Treloar. The process of fitting the theoretical curves to the experimental points constituted a determination of Young's modulus E for each rubber specimen. As a check on the experimental results, and also on the theory employed, determinations of E were also made by two additional methods, namely, from rough stess-strain curves, and from the relation $E = 3\gamma\rho RT/M_c$. With one exception, the internal agreement between the three determinations of E for the four different samples was satisfactory. The exception noted can probably be ascribed to the use of too small a value of M_c for the sample of lowest chain molecular weight.

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MECHANICAL BEHAVIOR OF A POLYMER AT TEMPERATURES THROUGH THE GLASS TRANSITION TEMPERATURE *

J. R. Stevens and D. G. Ivey

Department of Physics, University of Toronto, Toronto, Canada

INTRODUCTION

The glass transition in polymeric materials has been a source of investigation for the past twenty years. Questions concerning its thermodynamic nature and molecular origin are still being investigated[1–8].

In the belief that such data would contribute useful information to the problem of the transition, measurements of the variation of stress with temperature at constant elongation and the variation of length with temperature at constant stress were made through the rubberlike, transition, and glasslike regions of a particular polymer.

These measurements were made on Paracril-35, a copolymer of butadiene and acrylonitrile, containing 35% of the latter. The samples were obtained from the Polymer Physics Laboratory of the University of Notre Dame. This copolymer was selected because its properties of noncrystallization and negligible oxidation deterioration[9] made it particularly suitable for the type of measurements planned. Also, unlike many polymeric materials which are rubberlike at room temperature, its transition region occurs at a relatively high temperature ($\sim -25°$ C) so that the low-temperature limit of the apparatus does not prohibit the attainment of temperatures well into the glass region. It is hoped that the results obtained are representative of noncrystallizing polymers in general.

APPARATUS

Preliminary stress-temperature investigations were made using an apparatus consisting essentially of a balance arm, to one side of which the sample is attached and to the other side of which chains are suspended so that continuous adjustments of the stress on the sample are possible[10]. Even though the change in length of the sample in the balancing process is not more than a few thousandths of an inch, this change makes it impossible to make consistent measurements in the glasslike region. Consequently an apparatus using a strain gage as a stress measuring element was used. The apparatus is illustrated in Figure 1.

The sample S is contained in a rectangular brass box A with one large circular plastic end B. The box is enclosed in a system of concentric Dewar cans C and D. Mounted near the top of the box is an unbonded Statham strain gage F (type Gl-80-350). The gage has a range of ± 80 ounces, a maximum excitation voltage of 15 volts and a rated sensitivity of 32.45 microvolts (open

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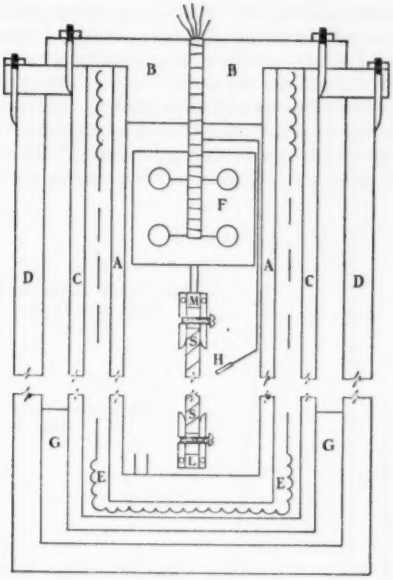

FIG. 1.—Stress-temperature apparatus for measurements made at constant elongation.

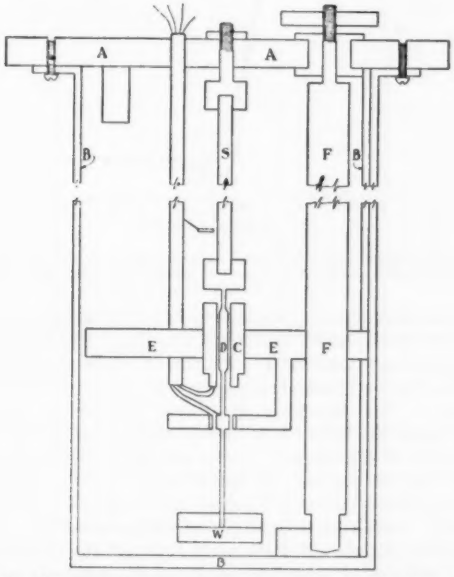

FIG. 2.—Length-temperature apparatus for measurements made at constant load.

circuit) per volt input per ounce. The change in length of the sample with movement of the arm of the strain gage is negligible. The sample is stretched between the base of the box and the arm of gage by means of clamps L and M. Liquid air G is introduced into the outer Dewar. Heat flow from the metal box is slowed by the inner Dewar and controlled by the heater coil E. Copper-constantan thermocouples H are used to measure the temperature. The temperature can be read to the nearest 5 microvolts ($\frac{1}{6}$° K) on a Brown recorder with a one millivolt full scale deflection. Temperature gradients down to 1° K

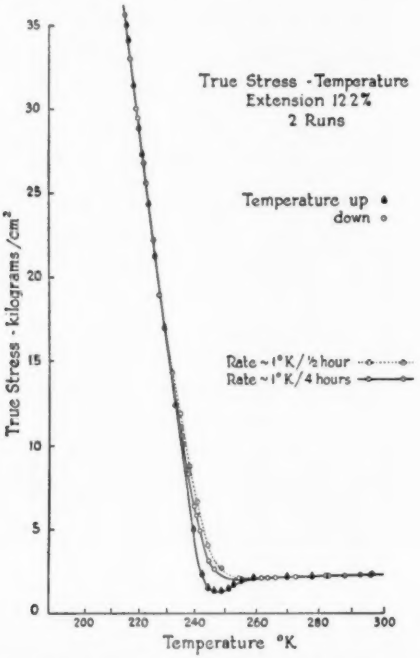

FIG. 3.—True stress vs. temperature (constant elongation) results for two runs at 12.2% extension. The change of behavior with change of temperature gradient in the transition region is shown.

in 4 or 5 hours can be obtained with this system. It is important to have temperature gradients which can be controlled and which can be made low since the discussions of the glass transition involve the question of equilibrium.

The apparatus used to make the length-temperature measurements is illustrated in Figure 2. The sample S is suspended from an insulating Bakelite plate A, which forms the top of a copper container B. A known weight W is attached to the end of the sample. A linear differential transformer coil C is mounted on a Plexiglas support E, which is in turn mounted on a very fine screw F, so that the transformer coil can be moved parallel to the sample length. The transformer is connected to a phase sensitive detector which indicates the direction of motion of a core D suspended between the end of the sample and the weight and centered in the transformer by means of electrical contacts.

The amount which the screw must be rotated to bring the detector reading to zero is a direct measure of the change in length of the sample. A change of 10^{-4} inch can be detected, although measurements were recorded to the nearest thousandth of an inch only. The cooling system is similar to that used in the stress-temperature work. Drying agents are included in both the length-temperature and stress-temperature systems to insure that the air surrounding the sample remains dry. Corrections are made for thermal expansion where necessary.

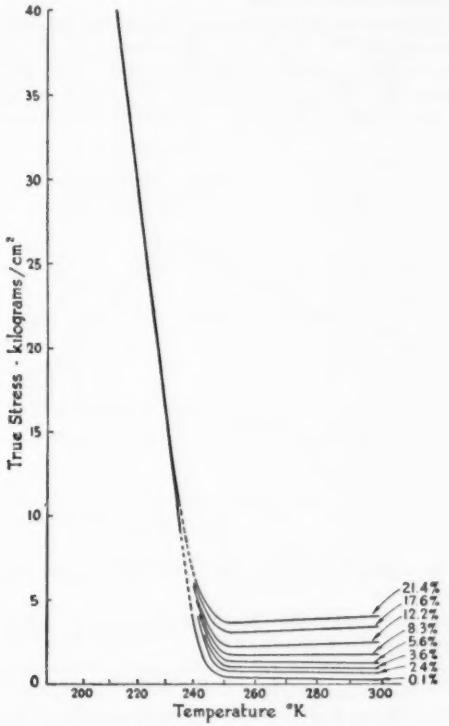

FIG. 4.—True stress vs. temperature (constant elongation) results for eight extensions from 0.1% to 21.4%. A unique behavior is shown in the glasslike region which is independent of the initial stress imposed over a wide range of temperature gradients.

RESULTS

With the temperature gradients used, each experimental run extended over a period of several days. For each extension at least two runs were made.

The results for a typical stress-temperature experiment for 12.2% extension are shown in Figure 3. The force per unit extended cross-sectional area (i.e., the true stress) is plotted against temperature. In Figure 3 the results of two successive runs are plotted showing the reproducibility of the data in the rubber-like and glasslike regions, and the dependence on temperature gradient in the

transition region. In general gradients of about 1° K in 2 hours were used in the rubberlike and the glasslike regions and gradients down to 1° K in 4 hours were used in the transition region. Figure 4 shows the average stress-temperature curves for eight extensions, ranging from 0.07% to 21.4%. These curves show a unique behavior in the glasslike region, independent of the original stress imposed and independent of the rate at which the temperature was changed through the transition region within the ranges of temperature gradients used in this work. Details of the behavior in the rubberlike region are shown in Figure 7 on an expanded stress scale.

Figure 5 is a typical set of length-temperature measurements showing two experimental runs at 10.3% extension. The same rates of temperature change as for stress-temperature measurements were used. The average length-temperature curves for eight different stresses, which gave extensions ranging from 2.3% to 22.7%, are shown in Figure 6. (Measurements were actually made at

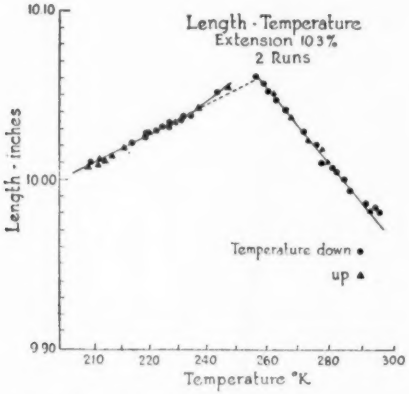

FIG. 5.—Length vs. temperature (constant stress) results for two runs at 10.3% extension.

constant load but were converted to constant stress.) Compensating expansions in the apparatus made it unnecessary to correct the length-temperature results for apparatus expansion. If the transition temperature is assumed to be the temperature of the intersection of the straight line portions in the rubberlike and glasslike regions, a shift in the transition temperature with extension occurs. Also the transition temperatures defined in this way are different for the length-temperature and stress-temperature results as a whole.

DISCUSSION

The stress-temperature and length-temperature results in the rubberlike region, shown in Figures 6 and 7, were compared internally and with each other by using the equation of state as obtained from the kinetic theory of rubberlike elasticity. The equation used is[11]

$$Z = KT\left[L - \frac{1 + \alpha(T - T_0)}{L^2}\right] \tag{1}$$

where Z is the nominal stress extending a sample, which is a unit cube at a reference temperature T_0, to a length L at a temperature T. The quantity K, which depends on molecular factors, and the quantity α, which is the volume coefficient of thermal expansion, were taken as parameters and were determined for each of the stress-temperature and length-temperature curves at a temperature $T = T_0 = 293°$ K. The results are shown in Tables I and II. The

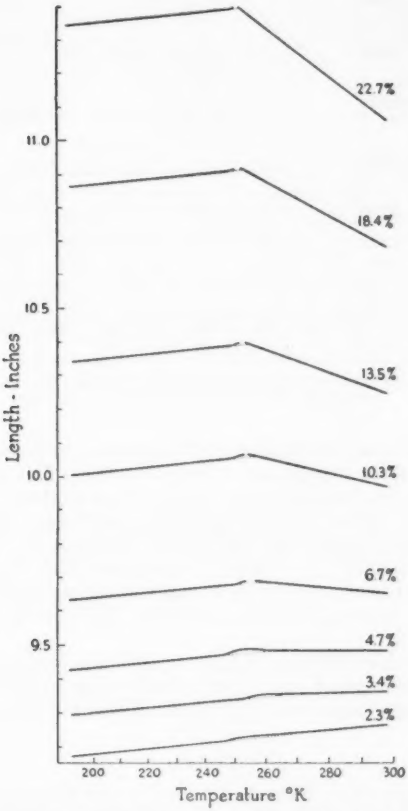

FIG. 6.—Length vs. temperature (constant stress) results for eight stresses which yield extensions from 2.3% to 22.7%.

average value of α obtained from the stress-temperature curves is 5.55×10^{-4}/° K and from the length-temperature curves is 6.01×10^{-4}/° K. The average value of K obtained from the stress-temperature curves is 24.2 g/cm^2 degree K and from the length-temperature curves is 22.9 g/cm^2 degree K. These results agree with those calculated from the data of Baldwin, Ivory, and Anthony[11] for stress-temperature measurements on this same material, for small extensions in the rubberlike region. However, there is a considerable spread in the results,

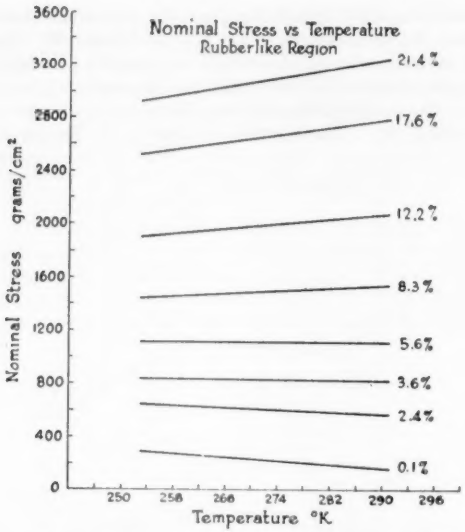

FIG. 7.—Nominal stress vs. temperature (constant elongation) results in the rubberlike region for eight extensions from 0.1% to 21.4%.

the calculated value of α increasing as the extension increases. This variation is an indication of the limitations of Equation (1), which is known to inadequately represent the internal energy contribution to stress.

In the glasslike region, a linear expansion coefficient $1/L(\partial L/\partial T)_z$, can be calculated from the length-temperature data of Figure 6. The average value obtained is $8.58 \times 10^{-5}/^\circ$ K. Using this value and the slope of the line in the glasslike region in Figure 4 a value of Young's modulus can be calculated. This gives 1.58×10^{10} dynes/cm^2 for this material. Both of the values are normal for a glass.

The shift in transition temperature to lower temperatures with increasing extension shown in Figure 6, and observed previously by other workers[7], can be interpreted as supporting the isofree volume concept of the transition. If it is

TABLE I

VALUES OF THE MOLECULAR FACTOR, K, AND VOLUME EXPANSION COEFFICIENT, α, CALCULATED FROM DATA FROM THE NOMINAL STRESS VS. TEMPERATURE RESULTS OF FIGURE 7 FOR EIGHT EXTENSIONS USING EQUATION (1)

Extension %	Calculated K g/cm² degree K	Calculated $\alpha \times 10^4/^\circ$ K
21.4	20.7	6.81
17.6	21.1	6.07
12.2	22.9	5.45
8.28	23.5	5.25
5.64	26.7	6.40
3.59	27.2	4.64
2.44	27.7	4.89
0.07	23.9	4.85

TABLE II

VALUES OF THE MOLECULAR FACTOR K AND VOLUME EXPANSION COEFFICIENT α, CALCULATED FROM DATA FROM THE LENGTH VS. TEMPERATURE RESULTS OF FIGURE 4 FOR EIGHT EXTENSIONS USING EQUATION (1).

Extension %	Calculated K grams/cm² degree K	Calculated $\alpha \times 10^4$/° K
22.7	20.8	8.31
18.4	21.0	7.43
13.6	22.4	7.29
10.3	22.0	5.20
6.72	22.9	5.13
4.72	23.7	5.39
3.44	24.7	4.56
2.29	25.6	4.80

considered that a certain minimum volume is required by the polymer system before the transition begins, then since the sample is slightly compressible this minimum volume would occur at lower temperatures as the extension increases, shifting the transition temperature. In a quantitative investigation of this, the change in volume of the sample on extension was measured and was expressed in terms of Poisson's ratio, σ, defined as the ratio of the transverse to the longitudinal strain. The results are shown in Figure 8 which compares the measured value of σ for Paracril-35 with that for an incompressible material. Knowing σ and the volume expansion coefficient α the shift in transition tem-

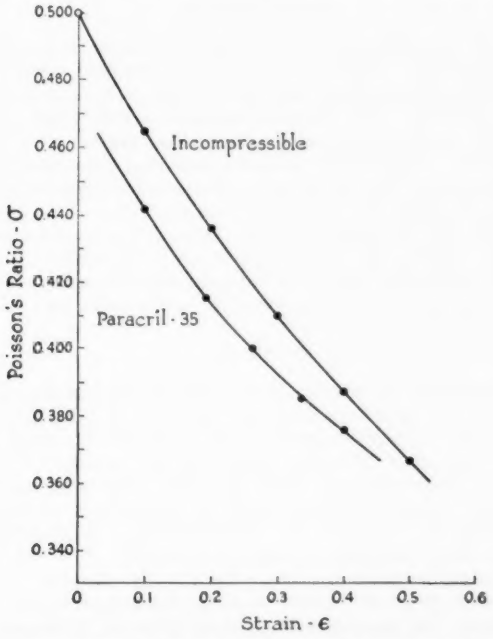

FIG. 8.—Poisson's ratio σ vs. strain for an incompressible sample and Paracril-35.

perature corresponding to a given change in extension can be calculated and gives values in rough agreement with the observed shift. This shift is not observed in the stress-temperature work since the normal volume contraction of the sample is hindered because the sample is maintained at constant length.

The transition temperatures appear to be different in the stress-temperature than in the length-temperature work. Kauzman[8] points out that the mechanism responsible for the onset of the transition in the two cases could be quite different because of the different ways of treating the sample during experimental measurements. This would lead to different transition temperatures and also emphasizes the possibility of more than one mechanism being responsible for the transition. On the other hand it is not entirely clear what should be called the transition temperature in the two cases. It is noticeable from the results that the transition regions, that is the regions in which markedly time-dependent physical properties are observed, extend over the same temperature range in both cases.

In the glasslike region, the temperature was held constant for periods of time up to 12 hours. No changes in the measured lengths and stresses were observed. Also in both cases the behavior in the glasslike region could be reproduced by changing the temperature within this region or by repeating the whole experiment. Moreover any temperature gradient within the range obtainable by the apparatus could be used and no change in behavior detected except in the transition region.

CONCLUSION

This research was undertaken to investigate the nature of the glass transition in polymeric materials. While many workers in the field attribute the transition to rate effects, this research provides no support for this view. A unique behavior was observed in the glasslike region for a wide range of temperature gradients. This tends to support the theoretical arguments put forward recently by Gibbs and DiMarzio[12] which indicate that a second-order transition does exist. They state that the glass transition is the experimental manifestation of the second-order transition, but that the value of the glass transition temperature will not necessarily be the value of the second-order transition temperature for experiments performed on a finite time scale. Since in experiments of the type reported here it is not clear what should be called the glass transition temperature, this approach seems very reasonable.

SUMMARY

Stress-temperature (constant strain) and length-temperature (constant stress) measurements have been made on Paracril-35 (a butadiene-acrylonitrile copolymer) in the temperature range −80° C to 25° C, which includes the glasslike, transition, and rubberlike states for this material ($T_g \sim -25°$ C). Time effects are observed in the transition region, but for temperature gradients used (down to about 1° C in 4 hours) the behavior at low temperatures is unique, indicating the existence of a real transition. This behavior is independent of the strain imposed at room temperature. The shift in transition temperature (in the length-temperature work) with extension is found to give quantitative support to the theory that the transition occurs at a certain minimum volume. In the rubberlike region, behavior is represented by the usual equation of state.

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THERMOPHYSICAL CHARACTERISTICS OF CURED RUBBER STOCKS *

V. I. Gengrinovich and V. O. Fogel

Scientific Research Institute of the Tire Industry

The thermophysical characteristics of vulcanizates (their thermal conductivity λ in kcal/meter-degree-hour and their volumetric heat capacity $c\alpha$ in kcal/m^3-degree, as well as the characteristics derived from these—the thermal diffusivity $a = \frac{\lambda}{c\alpha}$ m^2/hour and the thermal activity $\epsilon = \sqrt{\lambda c\alpha}$ in kcal/m^3-degree-hour[1]) are important for thermal calculations on rubber parts and in the study of the processes occurring during the vulcanization of rubber. The thermal conductivity of vulcanized stocks has a definite influence on the service life of passenger tires.

Little data have been published in the literature in regard to results of experimental determinations of these characteristics. The majority of the experiments on thermal conductivity of vulcanizates were conducted by the method of stationary heating conditions, which requires a prolonged (6–12-hour) uniform preliminary heating of the samples and the use of complex compensation devices (to prevent heat losses).

The methods used for determining the thermophysical characteristics of vulcanizates in the Moscow Institute of Chemical Machine Construction are relative ones. They require preliminary tests of the thermophysical characteristics of the standard medium with which the samples come in contact, and the use of a fairly complex apparatus for the accurate recording of the duration of the heat impulse, which is given off for a period of 1–2 seconds[1].

The most promising methods for the study of the thermophysical characteristics of rubber vulcanizates are the present-day absolute velocity methods, based on nonstationary thermal conditions (the methods of heat probes under regular conditions).

In the probe method, heat probes of constant capacity are introduced between the samples to be tested, thus making possible a simultaneous determination of thermal conductivity and volumetric heat capacity of the samples. These methods have not yet won sufficient approval in the testing of vulcanizates[2].

The study of the thermophysical characteristics of vulcanizates by the methods of regular conditions, developed by Prof. G. M. Kondratev[3], is of great interest; but for the determination of thermophysical characteristics of materials which conduct heat poorly, including vulcanized rubbers, it is absolutely necessary to make sure of a number of boundary and time conditions, since otherwise the experimenter might arrive at erroneous conclusions.

Methods involving regular conditions are based on the heating or cooling of bodies in a medium whose temperature t_f and coefficient of heat emission from the surface of the body to the surrounding medium α remain constant. For the

* Translated by Malcolm Anderson from *Kauchuk i Rezina*, Vol. 16, No. 4, pages 27–32 (1957).

determination of thermal diffusivity of vulcanizates by methods involving regular conditions, the samples used are usually in the shape of a sphere in the center of which is located the hot junction of a thermocouple for the measurement of the temperature t_c at the center of the sphere. If the initial temperature of the sphere t_0 was a constant, then the temperature in the center of the sphere for a period of time τ after the commencement of heating or cooling depends on the following values[4]:

$$\theta_c = \frac{t_f - t_c}{t_f - t_0} = f(F_0, Bi) \tag{1}$$

where $F_0 = \frac{a\tau}{R^2}$ is the Fourier criterion, depending on the coefficient of thermal diffusivity a of the sphere material, the duration of heating or cooling τ and the radius of the sphere R;

$Bi = \frac{\alpha R}{\lambda}$ is the Biot criterion, depending on the coefficient α of thermal emission from the surface of the sphere to the surrounding medium, the coefficient of thermal conductivity λ of the sphere material and the radius R of the sphere.

Equation (1) is an infinite converging series. For example, for the center of the sphere:

when $Bi = \infty$,

$$\theta_c = 2 \sum_{n=1}^{\infty} (-1)^{n+1} e^{-n^2\pi^2 F_0} \tag{2}$$

and when $Bi = 1$,

$$\theta_c = \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{2n-1} e^{-\left[(2n-1)\frac{\pi}{2}\right]^2 F_0} \tag{3}$$

With the values of $1 \leqq Bi \leqq \infty$ and $F_0 \geqq 0.2$, a regular system comes about, in which it is satisfactory to limit the series to its first term with an accuracy of the order of 0.5%, and an experimental relation is established between the value θ_c and the Fourier criterion. For example, for the center of the sphere, when $F_0 \geqq 0.2$:

when $Bi = \infty$,

$$\theta_c = 2e^{-\pi^2 F_0} \tag{4}$$

and when $Bi = 1$,

$$\theta_c = \frac{4}{\pi} e^{-\frac{\pi^2}{4} F_0} \tag{5}$$

With values of the Fourier criterion less than 0.2, the exponential relation changes into a more complex one, and the omission of the terms of the series subsequent to the first one may lead to serious errors.

Table I and Figure 1 give values of θ_c when $Bi = \infty$ as a function of the Fourier criterion, calculated with the exact Equation (2) and with the exponential relation (4).

TABLE I

VALUES OF THE QUANTITY $\theta_c = \frac{t_f - t_c}{t_f - t_0}$ AS A FUNCTION OF THE FOURIER CRITERION WHERE $Bi = \infty$

$F_0 = \frac{a\tau}{R^2}$	0.04	0.05	0.06	0.07	0.08	0.09	0.10	0.11	0.12	0.13	0.14	0.15	0.2	0.25
θ_c	0.986	0.967	0.925	0.880	0.825	0.766	0.707	0.649	0.595	0.543	0.494	0.460	0.278	0.170
$2e^{-\pi^2 F_0}$	1.347	1.221	1.106	1.002	0.908	0.823	0.745	0.675	0.612	0.555	0.502	0.456	0.278	0.170

These data show that the value of the quantity θ_c calculated with the equation for regular conditions (Equation (4)), where $F_0 \leqq 0.07$, are greater than unity, which can be true only when $t_c < t_0$ and thus contradicts the initial condition.

It follows from the above that for the heating of a rubber sphere in boiling water ($t_f = 100°$ C) in which the coefficient of heat emission α is very great and for which $Bi = \infty$ may be assumed, only those experimental data for which $F_0 \geqq 0.2$ and $\theta_c = \frac{100 - t_c}{100 - t_0} \leqq 0.278$ can be processed by a method of regular conditions. Taking the initial temperature of $t_0 = 20°$ C, we obtain the value of the minimum temperature at the center of the sphere, where regular conditions prevail

$$t_c \geqq 100 - 0.278\ (100 - 20) \cong 80° \text{ C}$$

The equations presented, (3) and (5), make it possible to determine the error which results if the rubber sphere is cooled in a medium of air with regular conditions, and the experimental data are processed with the aid of tables compiled for the value of the criterion $Bi = \infty$. Such an experimental error was admitted by L. S. Frumkin and Yu. B. Dubinker in their study of the thermal diffusivity of rubber stocks[5]. In their experiments the radius of the sphere was $R = 0.03$ meter, the coefficient of heat emission from the surface of the sphere into the freely moving air may be estimated as of the order of $\alpha \cong 10$ kcal/m²-degree-hour, and the coefficient of thermal conductivity of the

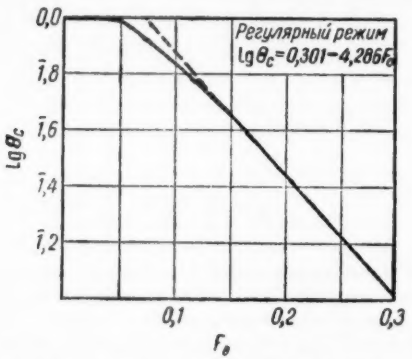

FIG. 1.—Relation of θ_c to the Fourier criterion for a sphere where $Bi = \infty$. The abscissa represents F_0, the ordinate $\log \theta_c$. The legend at top right reads: Regular conditions/$\log \theta_c = 0.301 - 4.286\ F_0$.

rubber stocks did not exceed $\lambda = 0.3$ kcal/m-degree-hour. Hence for the experiments mentioned

$$Bi = \frac{\alpha R}{\lambda} \cong \frac{10 \times 0.03}{0.3} = 1; \text{ not } Bi = \infty$$

Relative calculations made with Equations (3) and (5) have shown that the values of the thermal diffusivity coefficients given in the paper mentioned above for the values t_c = 120–30° C are 1.78–3.39 times too low, and hence the authors' conclusion that the thermal diffusivity of all rubber stocks increases with temperature does not follow at all from their experimental data. An analogous critique of the conclusions of Frumkin and Dubinker was given by Cuthbert[6] and Rehner[6].

In the present work the thermophysical characteristics of industrial vulcanizates are determined by the following methods:

(1) Thermal diffusivity of the stocks (a) by the method of regular conditions;
(2) Specific heat of the stocks (c) by calorimetry;
(3) Specific gravity of the stocks (γ) by means of a pycnometer;
(4) The thermal conductivity (λ) of the stocks is calculated by the equation

$$\lambda = ac\gamma \tag{6}$$

A brief description of each of these methods is given below[7].

For the determination of the thermal diffusivity of the rubber vulcanizates, the temperature in the center of the sphere was measured during the process of being heated in boiling water. The samples of the stocks were prepared by vulcanization in hemispherical molds with diameters of 59 and 63 mm. A thermal electrode (a copper wire with a diameter of 0.4 mm and a constantan wire with a diameter of 0.2 mm) was passed through the depth of one hemisphere with the aid of a hypodermic needle. The ends of the wires were welded together in an electric arc and the hot junction of the thermocouple was placed in the center of the sphere. A self-vulcanizing rubber cement was used to cement the rubber hemispheres together. The cemented hemispheres were bound together tightly with cord and kept at room temperature not less than 24 hours. In some cases the spheres were exposed to heat for several hours (70° C) for better bonding.

Before the start of the experiment the samples tested were kept for a long period in a constant-temperature water bath at a temperature of 20 ± 0.02° C. After this the samples were quickly plunged into a glass flask (volume about 4 liters) filled with boiling water. During the period of the experiment the sphere was kept in the central part of the flask by means of cords and a weight was hung on the samples with a specific gravity less than one. The flask was equipped with a reflux condenser, and the water in it was kept at boiling during the course of all the experiments.

During the experiment, the thermoelectromotive force in the thermocouple, whose hot junction was placed in the center of the sample and whose cold junction had a temperature of 0° C, was measured with the aid of a potentiometer of the PP type at regular intervals of time (once every 2–3 minutes at the start of the experiment and every 5–10 minutes at its conclusion). The thermoelectromotive force in the thermocouple was converted to ° C with a calibration

curve and in this way the temperature in the center of the rubber sphere was determined.

Figure 2 shows (with the data of one of the experiments) the change in temperature at the center of the sphere as a function of the duration of heating. The duration of the experiment in minutes is plotted on the abscissa axis, the natural logarithm of the difference between the temperature of boiling water t_f and that of the center of the sphere t_c on the ordinate axis. Figure 2 shows that, in accordance with the equation for regular conditions (Equation (4)), there is a fixed linear relation during the experiment between the quantity $\ln (t_f - t_c)$ and the duration of the heating τ. Determining the tangent of the

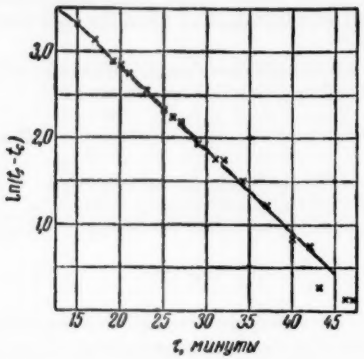

FIG. 2.—Natural logarithm of the excess temperature in the center of the sphere as a function of the duration of heating (Stock 2R21). The abscissa represents time τ in minutes, the ordinate $\ln(t_f - t_c)$.

angle of inclination of the straight line with relation to the abscissa axis from the experimental points (which, as noted above, correspond to $t_c \geqq 80°$ C), on the basis of Equation (4) we obtain (4a) where $tg = \tan$:

$$\ln(t_f - t_c) = \ln [2(t_f - t_0)] - \frac{\pi^2 a}{R^2} \tau = \text{const} - \text{tg}\, \beta \cdot \tau \qquad (4a)$$

A special analysis has shown that the first term of this equation depends to a large extent on the initial heating conditions of the sample. However, for a determination of the coefficient of thermal diffusivity by the method of regular conditions it is quite sufficient merely to know the rate of cooling $m = \tan \beta$, since

$$a = m \left(\frac{R}{\pi} \right)^2 \qquad (7)$$

The technique of determining the thermal diffusivity by the method of regular conditions thus consists of a graphic expression of the experimental data in coordinates of $\ln (t_f - t_c)$ and τ, and a determination of the angle of inclination of the linear portion of the lines obtained to the abscissa axis.

The specific heats of the raw rubbers, the ingredients and the vulcanized stocks were measured with a platinum calorimeter[8]. The samples, in the form of finely cut up pieces or powders, were heated with a constant current under

TABLE II

RECIPES AND VULCANIZATION CONDITIONS OF VULCANIZED STOCKS TESTED *

Ingredients, parts by weight	Stock numbers										
	3	5	42PV	43PV	4E31	2R210	1	2E45	46PV	4	4E–46
SKB-50 sr	100	100	100	100	—	—	—	—	—	—	—
SKB-50 sv	—	—	—	—	100	—	—	—	—	—	—
SKB-P-50r	—	—	—	—	—	120	—	—	—	—	—
Natural rubber, unplasticized	—	—	—	—	—	—	100	—	—	—	—
Natural rubber, plasticized	—	—	—	—	—	—	—	100	—	—	—
Buna-S-3	—	—	—	—	—	—	—	—	—	100	—
SKS-30 (plasticity 0.44–0.50)	—	—	—	—	—	—	—	—	—	—	100
Kok-saghyz	—	—	—	—	—	—	—	—	100	—	—
Stearic acid	2.5	2.5	—	—	—	—	0.5	2.0	—	0.5	—
Rubrax	—	5.0	—	—	—	5.0	—	2.0	—	—	—
Ishimbaev black oil	—	—	2.5	2.5	6.0	6.0	—	—	2.5	—	5.0
Oleic acid	—	—	2.0	2.0	2.0	1.5	—	—	2.0	—	2.0
Petrolatum	—	—	—	—	—	—	—	—	—	—	5.0
Paraffin	—	—	1.0	1.0	1.0	—	—	—	1.0	—	—
MBT	1.8	1.8	—	—	1.5	0.8	0.7	—	—	0.7	—
MBTS	—	—	0.4	0.4	—	—	—	0.6	0.4	—	1.0
TMTD	—	—	0.2	0.2	—	—	—	—	0.2	—	0.4
Diphenylguanidine	—	—	—	—	—	1.0	—	0.6	—	—	—
Zinc oxide	5.0	5.0	5.0	5.0	5.0	—	5.0	5.0	5.0	5.0	5.0
Calcined magnesia	—	—	—	—	—	5.0	—	—	—	—	—
Carbon black:											
Channel	—	60	—	—	45	—	—	—	—	—	40
Thermal	—	—	—	—	20	—	—	—	—	—	20
Oil black (Nozzle black)	—	—	50	70	—	45	—	30	—	—	—
Furnace	—	—	—	—	—	—	—	—	50	—	—
Aldol	—	—	—	—	—	—	—	0.5	—	—	—
Rosin	—	—	—	—	—	—	—	3.0	—	—	1.0
PBNA	—	—	—	—	1.0	1.5	—	1.5	—	—	—
Sulfur	1.5	1.5	3.0	3.0	2.5	2.3	3.0	2.5	3.0	3.0	1.7
Vulcanization temperature, ° C	143°	143°	143°	143°	143°	138°	143°	138°	143°	143°	143°
Vulcanization period, minutes	75	60	60	60	65	60	60	45	60	60	65
Diameter of spheres, mm	63.3	63.3	58.9	58.9	58.9	58.9	63.3	58.9	58.9	63.3	58.9

* Samples of stocks 42PV, 43PV and 46PV were supplied by E. A. Pakhomova.

conditions such that there was no loss of heat. The amount of energy consumed in heating the sample plus the calorimeter was measured by a compensation method. The temperature rise was observed with a Beckmann thermometer. The specific heat was calculated with the equation:

$$C = \frac{Q}{G\Delta t} - \frac{W_k}{G} \tag{8}$$

where Q is the amount of energy in calories; G is the weight of the sample in grams; Δt is the rise in temperature in ° C; and W_k is the water equivalent of the empty calorimeter.

15–20 g of the rubber or vulcanizate, 25 g of sulfur and 9–12 g of carbon black were placed in the calorimeter. The temperature was raised by about 1° C, the duration of heating was 10–15 minutes. The experiments were carried out at room temperature, and the specific heat was determined on each sample 3–5 times.

The specific gravity was determined with a pycnometer of 25 ml volume. The liquid used for filling it was ethyl alcohol; the specific gravity of the carbon black was also determined, but in a xylene medium. The samples of rubbers and vulcanizates were kept under a vacuum for a long period and then the

TABLE III

HEATING RATE m AND THERMAL DIFFUSIVITY a OF THE VULCANIZATES STUDIED

	Stock number										
	3	5	42PV	43PV	4E31	2R210	1	2E45	46PV	4	4E46
$m \times 10^3$ min^{-1}	51	77	102	122	102	96	42	76	93	79	109
$a \times 10^4$ m^2/hr	3.1	4.7	5.8	6.4	5.4	5.1	2.6	4.0	4.9	4.8	5.8

alcohol was poured into the vacuum. The filled pycnometer was kept at 20° C. The volume of the liquid was kept constant at this temperature by means of the liquid level in a capillary with a diameter of about 1 mm. During weighing the capillary was closed with a ground-glass cap.

The materials tested were vulcanizates prepared with a base of natural, polybutadiene (SKB) and butadiene-styrene (SKS) rubbers, with standard recipes, as well as industrial stocks of the tread, breaker and carcass types. The recipes of the stocks and their vulcanization conditions are given in Table II.

The results of the processing of the experimental data by the method of regular conditions are given in Table III, in which the rates of heating and the thermal diffusivities of the stocks tested are given.

Since, as has been shown above, the regular conditions existed at temperatures of 80–100° C at the center of the sphere, the values of a presented in Table III belong to this range of temperatures.

Table III shows that the thermal diffusivity of the stocks tested varies by a factor of about 2½, depending on their composition. Natural rubber stocks, whether pure (No. 1) or loaded (No. 2E-45) are characterized by lower coefficients of thermal diffusivity than stocks of polybutadiene and butadiene-styrene rubbers.

No detailed study was made of the effect of the separate ingredients on the thermal diffusivity of stocks as a part of this undertaking. It is nevertheless sufficiently certain from the data obtained that carbon black raises the thermal

diffusivity considerably, and that the type of carbon black has a marked effect on this also. Thus in a vulcanizate prepared on a base of SKB-50 sr, channel black causes an increase of 50% on the thermal diffusivity (Nos. 3 and 5), while an oil black (nozzle black) incorporated in the same amounts (60 parts by weight on 100 of rubber) increases the thermal diffusivity to approximately twice as much (Nos. 42PV and 43PV). Oil black has an analogous effect in natural rubber stocks: 30 phr of oil black increases the thermal diffusivity of the vulcanizates to approximately 1½ times as much (Stocks Nos. 1 and 2E-45). The increase in the thermal diffusivity of vulcanized stocks containing oil black

TABLE IV

SPECIFIC HEAT AND SPECIFIC GRAVITY OF STOCKS TESTED

Stock no.	Specific heat, kcal/kg-degree	Specific gravity, kg/m³	Volumetric heat capacity, kcal/m³-degree
3	0.469	960	450
5	0.381	1150	438
4EPV	0.368	1179	434
4E31	0.381	1157	441
2R-210	0.406	1091	443
1	0.446	974	434
2E45	0.399	1079	430
46PV	0.372	1156	430
4	0.373	1176	439
4E46	0.367	1185	435

is likewise confirmed by results obtained for stocks 4E-31 and 2R210. The thermal diffusivity coefficients of these two stocks are close together, although the first contains 65 phr of carbon black (45 phr of channel black and 20 phr of thermal black) and the second 45 phr of oil black. The conclusion that oil black imparts to vulcanizates a higher thermal diffusivity than channel black is in accord with data from the literature[9].

The data obtained in this work of the specific heat C and the specific gravity γ of the stocks tested are given in Table IV.

A noteworthy fact is that, as the last column of Table IV shows, the volumetric heat capacities $C\gamma$ of all the stocks tested are close together (430–450

TABLE V

THERMAL CONDUCTIVITY OF RUBBER STOCKS

Stock no.	3	5	43PV	4E31	2R210	1	2E45	46PV	4	4E46
λ, kcal/m-hr-degree	0.140	0.205	0.279	0.238	0.225	0.113	0.173	0.211	0.212	0.250

kcal/m³-degree) although the specific heat and specific gravity values of the separate types of stocks are substantially different. Besides this, the volumetric heat capacity value of the vulcanized stocks differ little from those of their original raw rubbers[10]. This is explained by the fact that the principal ingredient of the vulcanized stocks besides the rubber itself, viz., the carbon black, with a low specific heat (C = 0.21 kcal/kg-degree) and a high specific gravity (γ = 1800 kg/m³), is characterized by a volumetric heat capacity which is close to the heat capacity of rubber.

As was noted above, the specific heat and specific gravity of the vulcanized stocks were determined at 20° C. Since the specific gravity decreases with an

increase in temperature, but the specific heat rises at the same time, the volumetric heat capacity should not undergo significant changes. This permits the use of the data of Table IV for calculating the thermal conductivity coefficient at 80–100° C of the stocks tested with Equation (6), with an accuracy sufficient for industrial calculations. The results obtained are given in Table V.

Since the volumetric heat capacity values of the stocks tested are close together, their thermal conductivities are practically proportional to their thermal diffusivities. Thus the relationship revealed previously regarding the effect of the composition of the stocks of their thermal diffusivities applies also to their thermal conductivities.

It is interesting to compare the data obtained in the present work for thermal diffusivity and conductivity with the data from the literature. Determinations of the thermal conductivity of vulcanizates by the method of stationary heat conditions, carried out by N. K. Mikhaĭlov, S. A. Polyak and S. B. Ratner may be considered the most reliable results (the accuracy of the determination of λ is estimated by the authors as ±1%). Table VI presents values of λ ob-

TABLE VI

THERMAL CONDUCTIVITY OF STOCKS, DETERMINED BY VARIOUS METHODS

Type of stock	λ, kcal/m-hr-degree	
	From the data of N. K. Mikhaĭlov et al.	Our data
Loaded vulcanizate based on SKB (polybutadiene rubber)	0.141	0.140
Loaded vulcanizate based on SKB (60 parts of channel black)	0.227	0.205*
Loaded vulcanizate based on natural rubber	0.188 (50 parts of channel black)	0.173 (30 parts of oil black)

* For a loaded stock based on SKB, containing 45 parts of channel black and 20 parts of thermal black, λ =0.238 kcal/m-hr-degree.

tained by the above-mentioned authors and ourselves. As Figure VI shows the results of determinations by the method adopted for the present work agree well with experimental data obtained by the stationary method. Unfortunately it is not possible to make an analogous compilation for thermal diffusivity. The data published in the literature on the thermal diffusivity of stocks were obtained by experiments so arranged that they do not correspond to our boundary conditions[11].

Rehner[12], in determining the thermal diffusivity, assumed unjustifiably that the surface temperature of the samples tested immediately assumes the temperature of the medium when these are plunged into boiling water. An analysis shows that when these temperatures have a difference of 0.5° C, the coefficient of thermal diffusivity obtained is 20% high. Backes[13] set up experiments with finite cylindrical samples, but processed the data with equations for an infinite cylinder, neglecting the heat output from the ends.

On the basis of the results of this work, the conclusion may be drawn that the use of methods of regular conditions for the determination of the thermophysical characteristics of vulcanizates is fully justified.

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THE INFLUENCE OF INTERMOLECULAR ACTION ON THE DYNAMIC FATIGUE OF RUBBERS *

V. E. Gul, D. L. Fedyukin, and B. A. Dogadkin

M. V. Lomonosov Institute of Fine Chemical Technology, Moscow, USSR

According to modern views the physical and mechanical properties of vulcanizates depend to a considerable extent on the degree of intermolecular action and a change in the character and degree of this action will alter mechanical properties.

The most convenient method of following intermolecular action is by swelling[1], since with this method any change in this action is not accompanied by a large change in the primary chemical valence forces. It has been shown[2] that the chemical nature of the solvent has considerable effect on the strength of the vulcanizate and that swelling is not necessarily accompanied by decreased tensile strength, but that in most systems studied the change in tensile strength passes through a maximum at certain values of the degree of swelling.

It has been shown[3] that natural rubber gum vulcanizates swelled by definite amounts of dibutyl phthalate and mineral oil have considerably greater fatigue resistance than the unswelled material under conditions of constant amplitude of deformation. The method of fatigue testing used in these experiments[2,3] was selected on the basis that fatigue resistance depends to a considerable degree on chemical properties but not on physical properties. It should be of interest to observe the influence of change in degree of intermolecular action on a large number of vulcanizates with different fatigue methods.

The physical mechanism of fatigue of unswelled vulcanizates by suitable fatigue tests has been studied[4,5]. In addition, as a result of the study of structure changes conclusions have been reached concerning the mobility of the space structure of vulcanizates of smoked sheet and butyl rubber during the fatiguing process, and also concerning the large role played by free radical reactions[6,8]. It should be remarked that the general proposal of B. K. Karmin and V. G. Epshtein[7], which considers the activation of the chemical process by heat developed within the fatigued sample[2], is still valid. An essential phenomenon appears to be the formation of free radicals[8] during the process of sample fatigue.

Deformation is inevitably accompanied by localized destruction of intermolecular bonds resulting in the formation of heat; that is, there is a relationship between modulus and internal friction[9,10]. Hysteresis, stress relaxation and heat formation are the result of destruction of secondary bonds. The accumulated heat is especially large during deformation of massive samples. The heat intensifies the chemical reactions that occur in the vulcanizate and directly influences its destruction during use. A change in structure can be observed during periodic deformation of a vulcanizate. This change depends to a considerable degree on the conditions of the experiment and is caused by

* Translated by Theodor Tarasjuk, Katherine and Willard P. Tyler for Rubber Chemistry and Technology, from *Kauchuk i Rezina*, Vol. 17, No. 9, pages 16–20 (1958).

chemical processes (oxidation, scorching, polymerization and others) and often by physical phenomena.

To determine the effect of a change in intermolecular action on the fatigue resistance of vulcanizates as tested by different methods, vulcanizates of rubbers differing in chemical composition and structure were tested. The rubbers used were smoked sheet; butadiene-styrene (70:30); butadiene-acrylonitrile (60:40, 74:26, 82:18). Fatigue resistance was evaluated by the number of deformation cycles from the start of the test to destruction of the sample. As solvents for the vulcanizates the following materials, differing from each other by length of hydrocarbon chain and by polarity, were used: dimethyl phthalate (DMP), dibutyl phthalate (DBP), dioctyl phthalate (DOP), dibutyl sebacate (DBS), dioctyl sebacate (DOS) and mineral oil (MO).

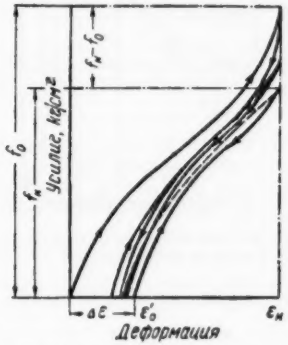

FIG. 1.—Change of stress and deformation of a vulcanizate during fatigue under conditions of constant final amplitude of deformation. Abscissa: Deformation. Ordinate: Stress, kg/cm².

To change the degree of intermolecular action on the rubber, vulcanizates containing carbon black were subjected to swelling. The degree of swelling was reported as per cent swell. The tests for fatigue resistance, conducted by the method of constant final amplitude of deformation, confirmed the previously reported[2] results. Dynamic fatigue was characterized by relative fatigue resistance (ratio of time for destruction of swelled sample to time of destruction of unswelled sample).

On comparing the fatigue resistance of rubbers which are under the same stress, high modulus rubber will be more favorably situated with respect to work required for stretching (per cycle) than will low modulus rubber. For rubbers with different modulus values the objective is to test under conditions of equal stress work per cycle of deformation. For determination of the quantity of stress work it is necessary to have a curve that gives the relationship between stress and deformation. On reaching dynamic equilibrium the amplitude of stress will change from 0 to f_k and the amplitude of deformation from ϵ_0 to ϵ_k (Figure 1). This relationship can be determined accurately enough on the fatigue machine the general principles of construction of which have been reported[11,12].

Testing the samples on such a machine at five to six different amplitudes of displacement of the device allows the determination of a quasi-equilibrium relationship between stress and deformation. The tests were conducted at room

temperature and at a frequency of 254 cycles per minute. As a rule the results of replicate tests fell on the same curve. A typical curve of stress-deformation under dynamic conditions for filled vulcanizates of SKN-40 is shown in Figure 2. The symbols ●, X, △, ○, correspond to the results of replicate tests.

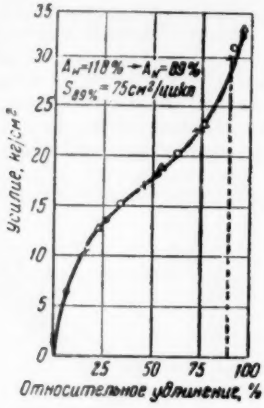

FIG. 2.—Stress-deformation curve for filled vulcanizate of SKN-40. Abscissa: Relative elongation, %. Ordinate: Stress, kg/cm². Legend on graph: $A_k = 118\% \rightarrow A_k = 89\%$, $S_{89\%} = 75$ cm²/cycle.

The amount of deformation is determined by the equation,

$$A_k = \frac{l' - l_0'}{l_0'} \cdot 100$$

where A_k = final, or steady deformation;

l_0' = the distance between marks on the sample at a definite stress established by the size of the loop (with clamps drawn together); and

l' = the distance between the marks on the sample at maximum swing of the clamps.

Under the indicated conditions the quasi-equilibrium stress value of fatigue samples is reached in a few minutes. Then, from a knowledge of the relationship between stress and deformation under dynamic conditions the testing can be conducted on the "Metallist MPS-2" machine at constant swing of the clamping device by selecting the proper values of the deformation for comparison under conditions of constant stress work per deformation cycle. In this case the stress work, which we call quasi-equilibrium work, was determined from the stress-deformation curve under dynamic conditions. The quantity of work is 0.0375 kg m per cycle. Under this condition the average time before destruction of different vulcanizates ranges from 15 minutes to 5 hours.

To compare different rubbers at the same value of stress work per cycle of deformation it is necessary to know at which starting amplitude of deformation the quasi-equilibrium work corresponding to the selected value is obtained. Since the stress-deformation curve for each vulcanizate was determined, it was

FIG. 3.—Change in relative fatigue resistance of filled natural rubber (NK) vulcanizates on swelling in DMP, DBP, DOP, DBS. Abscissa: Degree of swelling, %. Ordinate: Relative fatigue resistance. 1—●—Swelling in dimethyl phthalate; 2—○—Swelling in dibutyl phthalate; 3—×—Swelling in dioctyl phthalate; 4—△—Swelling in dibutyl sebacate.

easy to determine A_k as a deformation corresponding to a selected value of work. Then the amplitude of swing of the clamps necessary to obtain this A_k value can be determined. This will be the starting amplitude for the fatigue test.

The fatigue tests were conducted at room temperature and at 250 cycles per minute. Otherwise the conditions were identical to those used to obtain the stress-deformation curve. Accumulation of residual deformation was eliminated in the same manner as in the determination of the stress-deformation curve.

From Figures 3, 4 and 5, showing the results of testing by the above described method, it is seen that the fatigue resistance decreases with an increase in the degree of swelling, regardless of the vulcanizate-solvent combination used. To prove that such change in fatigue resistance on swelling is completely normal and is not due to excessively rugged conditions of the test, filled vulcanizates of natural rubber, swelled in dibutyl phthalate, were tested

FIG. 4.—Change in relative fatigue resistance of filled SKS-30 vulcanizates on swelling in DMP, DBP, DOP, DBS, DOS. Abscissa, ordinate and legend same as Figure 3, but add—5—■—Swelling in dioctyl sebacate.

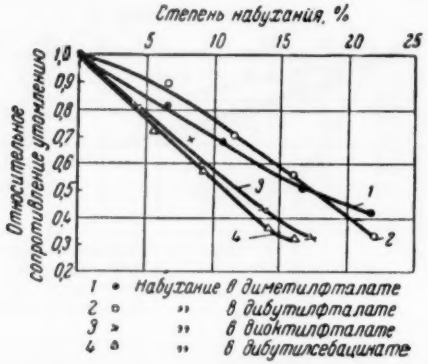

FIG. 5.—Change in relative fatigue resistance of filled SKN-40 vulcanizates on swelling in DMP, DBP, DOP, DBS. Abscissa, ordinate and legend same as Figure 3.

under conditions of equal stress work per deformation cycle. This allowed the test to be conducted under considerably more gentle conditions. The average time before destruction of sample increased considerably but the relative fatigue resistance did not change appreciably.

Thus, it appears that the steady decrease of fatigue resistance on swelling can be explained by a decrease in the amount of intermolecular action. This is also indicated by the change in the coefficient of mechanical loss[2] on swelling, glass temperature (Figure 6) and rebound (Figure 6a).

As shown by Figures 3–5, the rate of change of relative fatigue resistance on swelling the same vulcanizate in solvents containing various functional groups is different. On swelling a vulcanizate of nonpolar natural rubber in the slightly polar DBS, the fatigue resistance decreases very slowly with an increase in the amount of sorbed DBS, while a sharp drop in fatigue resistance takes

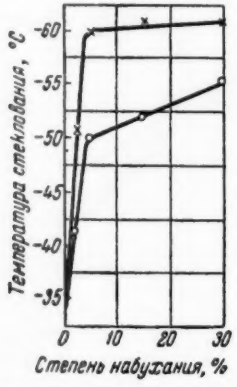

FIG. 6.—Change of glass temperature of filled vulcanizate of SKS-30 on swelling in MO—o and DBP—x. Abscissa: Degree of swelling %. Ordinate: glass temperature.

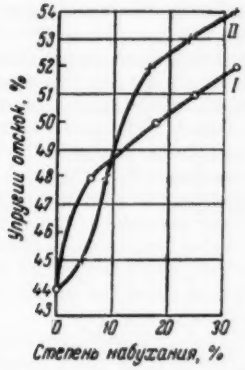

FIG. 6a.—Change in the value of elastic rebound on swelling vulcanizate of SKS-30 in MO—o and DBP—x. Abscissa: Degree of swelling, %. Ordinate: Elastic rebound.

place on swelling polar SKN-40 in the same solvent. The opposite effect is observed on swelling the same vulcanizates in the polar solvent, DMP.

Therefore the change in fatigue life of vulcanizates swelled in low molecular weight solvents depends not only on the degree of swelling but to a considerable extent on the nature of the solvent and the rubber. With natural rubber vulcanizates all of the phthalate esters decrease intermolecular action more than the sebacate esters. The aliphatic alcohol derived portion (alkyl group) of the solvent molecule has considerable effect on the change in degree of intermolecular reaction in the polymer. In general, an increase in the length of the alkyl chain decreases the degree of influence of the ester tested.

The weakening of intermolecular action with natural rubber vulcanizates (Figure 3) is greater, the higher the dielectric properties of the solvent. With vulcanizates of SKN-40 (Figure 5), on the contrary, the decrease in intermolecular action is intensified by a decrease in dielectric properties of the solvent. Therefore, it is apparent that the nature of the intermolecular action can con-

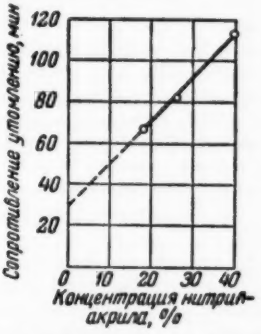

FIG. 7.—Change of fatigue resistance of gum vulcanizates of SKN as a function of acrylonitrile concentration. Abscissa: Acrylonitrile concentration, %. Ordinate: Fatigue resistance, minutes.

tribute to a decrease in the influence of low molecular weight components on the fatigue resistance of samples.

It is natural to expect that fatigue resistance must increase with an increase in intermolecular action in the polymer. To confirm this, vulcanizates of SKN-18, SKN-26 and SKN-40, which are characterized by different degrees of intermolecular action, were tested. The values of the equilibrium modulus for all three were the same, $E \approx 21.6 \pm 0.2$ kg/cm^2. Therefore the vulcanizates possessed equal degrees of crosslinking[13]. The results of the experiments, given in Figure 7, completely confirm the assumption that fatigue life increases steadily with an increase in intermolecular action. This once more confirms the correctness of the conclusion that, with a given method of fatigue test, fatigue resistance must steadily decrease with a decrease in the degree of intermolecular action in the polymer. The nature of the change in fatigue resistance under these conditions is not accidental.

Since fatigue under conditions of equal stress work per cycle of deformation was tested on thin samples (1.5 mm), in which the ratio of volume to surface is very low, the influence of change of heat loss to the surroundings with change in degree of swelling could be neglected. This is confirmed by the fact that the results which show the increase in fatigue resistance with increase in degree of intermolecular action (Figure 7) are in good agreement with data on change of static fatigue of the corresponding nitrile rubber vulcanizates.

It was interesting to find out if the direct relationship between static and dynamic resistance observed in the case of thin samples was preserved in the testing of production samples. For clarifying this point, production samples of gum vulcanizates of SKN-18, SKN-26 and SKN-40 were used. Testing of these gum vulcanizates on the Goodrich flexometer gave results of 235, 123 and 59, respectively. From these results it is seen that with massive samples the fatigue resistance decreases sharply with an increase in the concentration of acrylonitrile; that is, with an increase in the degree of intermolecular action.

The geometric ratio of volume to surface of the sample determines heat exchange with the surroundings. In testing massive samples the heat produced by internal friction leads to an increase in the temperature of the sample because of poor heat transfer. Internal friction, and consequently temperature, during the fatiguing process is directly connected with intermolecular action[2]. On testing thin samples the temperature is practically independent of the intermolecular action and is nearly equal to the temperature of the surroundings because of good heat transfer.

Thus it can be said that if thin samples are tested under conditions where $f_{max.}$ is constant, and with sufficiently large stress, the fatigue resistance is determined by the static fatigue (the same thing occurs with any test method if the stress is large enough). With massive samples under the same conditions, the fatigue resistance is determined by the amount of energy lost as a result of internal friction (the same thing is observed by any test method if the stress is small enough). Consequently, the mechanism of destruction of massive samples and thin samples of vulcanizates tested at constant work ($f_{max.}$ is constant in this case) differs.

It could be assumed that solvents which cause the sharpest drop in fatigue resistance when thin samples are swelled must cause the greatest increase in fatigue resistance when massive samples are swelled.

It is of interest to determine how the physical-mechanical properties of vulcanizates will change if equivalent quantities of solvents are added to the stock

before vulcanization. The samples were vulcanized in such a manner that the value of the quasi-equilibrium modulus was close to a selected value of $E'_{\infty} = 32$ kg/cm². The deflection used was equivalent to a stress of ± 2.5 kg/cm². The influence of functional groups and amount of softener on the fatigue resistance of plasticized vulcanizates then became clear. Figures 8 and 8a show that

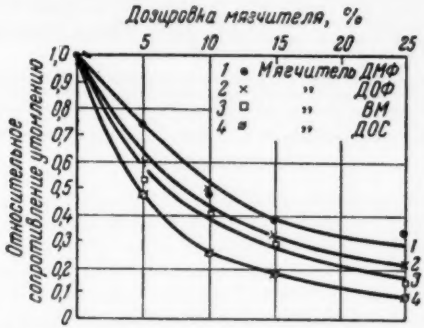

FIG. 8.—Dependence of fatigue resistance of filled vulcanizates of SKS-30 on the amount of softener. Abscissa: amount of softener, %. Ordinate: Relative fatigue resistance. Legend: 1—●—Softener DMP, 2—x—Softener DOP, 3—□—Softener MO, 4—ϕ—Softener DOS.

relative fatigue resistance steadily drops with an increase in the amount of plasticizer. The solvent here is active in the same manner as when it is used to swell vulcanizates.

Therefore, results obtained by swelling of vulcanizates could be used to characterize plasticized vulcanizates consisting of the corresponding vulcanizate-solvent combination. However, any influence of certain plasticizers on the chemical process taking place during vulcanization should also be considered.

FIG. 8a.—Dependence of fatigue resistance of filled vulcanizates of SKN-40 on the amount of DBS. Abscissa, ordinate, same as Figure 8.

CONCLUSIONS

The determination of the physical effect of softeners by an investigation of their influence on the swelling of vulcanizates is a convenient method for investigating the optimum composition of a compound which will produce given properties in the cured stock. This makes possible the improvement of such important properties of vulcanizates as fatigue resistance, mechanical loss, freeze resistance and others by using softeners with the appropriate functional groups.

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SCATTERING OF LIGHT IN CRYSTALLINE POLYMERS. I. FORMATION AND MELTING OF THE CRYSTALLINE PHASE IN NEOPRENE *

O. N. Trapeznikova and G. E. Smirnova

A. A. Zhdanov State University, Leningrad, USSR

INTRODUCTION

Several papers have recently appeared in the literature devoted to the study of the process of formation and melting of the crystalline phase in polymers by means of light scattering[1–3]. In these papers measurements of the angular distribution of the intensity of the scattered light from polymer films is described. It is assumed that knowledge of the angular intensity function should enable one to judge the size of the irregularities that cause the scattering.

However, existing theories of scattering are developed for isotropic particles; furthermore, theoretical conclusions concerning particle size are only possible in the case of single scattering. For any real crystalline polymer, we deal with a very large number of anisotropic particles, which are mostly of irregular shape and closely packed. Under these circumstances, single scattering is possible only in the initial stages of crystallization even in very thin layers, since in the completely crystallized polymer the distance between the crystals is very small (probably of the same order of magnitude as the wave length of the incident light). To clarify how far one is justified in applying theoretical deductions to anisotropic particles, more detailed investigation of the scattering phenomenon in relation to inherent properties of anisotropic particles is required. This had not been done before the present work was undertaken.

The ultimate purpose of our work was the study of the formation and melting processes of the crystalline phase of polymers. We were also interested in all aspects of the scattering phenomenon for anisotropic, spherical particles. Large particles scatter largely refracted light which must be mostly depolarized due to their anisotropy. Our observations were, therefore, made with polarized light. We measured separately the pattern of scattering corresponding to the the polarized and depolarized components of the scattered light. Besides, we filtered the polarized light from the transmitted beam and examined the depolarized light in the forward direction.

EXPERIMENTAL METHOD

Neoprene crystallizes at room temperature within several days; one can, therefore, follow all stages of its crystallization. It is essential to be able to prepare easily nonoriented neoprene films of any thickness. It is noteworthy that the shape of crystallites that we could observe with a microscope was generally irregular and one rarely succeeded in seeing regular spherical particles; they are generally of uniform size.

* Translated for Rubber Chemistry and Technology from *Optika i Spektroskopiya* 3, 631–637 (1957); *Cf. Chem. Abstr.* 52, 7754 f (1958).

Films of approximately 0.1 mm thickness were investigated as cast from solution. Neoprene, purified by multiple precipitation from alcohol was dissolved in benzene or carbon tetrachloride. The solution was poured into a frame placed on the surface of a pool of clean mercury. After most of the solvent had evaporated, the frame and film were lifted off the mercury and placed under high vacuum for several days for complete removal of the solvent. The film usually crystallized during this operation. In a film prepared in this manner, one can melt the crystals by warming and recrystallize by cooling. Exact data for the refractive index of neoprene were not available; the refractive index of an amorphous film is approximately 1.57 as determined by reflection. The mean refractive index of a strongly oriented film was determined by the immersion method as being about 1.6. The differences between the refractive index of the crystallites and the surrounding noncrystalline medium is therefore small, on the order of a few hundredth units.

The following technique was used in our investigation: the light from a hot filament lamp was passed through a monochromator which emitted only a narrow band of the spectrum; we chose the green region between 0.508 and 0.510 micron. The parallel light beam, limited by the slit of the monochromator, was passed through the polarizer (Arens prism) and then through the film under investigation which was placed in a vertical plane perpendicular to the incident beam. The light scattered by the film was passed through the analyzer into the photometer detector. To obtain a diagram of the scattering analogous to that obtained with nonpolarized light and to avoid the necessity of considering the dependence of the electric and magnetic vectors on direction, the plane of polarization of the incident light was set at a 45° angle to the plane of viewing. For the determination of the scattering pattern, the detector was moved in a horizontal plane in a circle around the film. A photoelectric tube FEU-19 was used as detector; with the amplifying tube, it constitutes one of the sections of a bridge circuit; the bridge was balanced by means of a pointer galvanometer. The linear dependence of the galvanometer reading on the incident light intensity was checked. The analyzer was placed before the detector and synchronized with it; the main parts of the analyzer were put in perpendicular positions, 45° to the plane of vision. Special precautions were taken to eliminate stray light. The light beam was 2 mm wide and 10 mm high, scattering volume, therefore, $10 \times 2 \times 0.1 = 2$ mm^3; the distance between film and photometer was 20 cm. The angular displacement of the detector was determined with a disc calibrated in degrees. In our experiments, divergence of the parallel beam was 6° on both sides of the center without a film and 10° with a film. In the determination of the angular variation of light intensity, corrections were included for the variations of the visual scattering volume and for scattering due to light refraction at the polymer-air interface. Other corrections were not made[3]. Light scattering measurements above room temperature were made with the film placed in special, heated, cylindrical glass containers. The heater was mounted on the table on which the film was mounted; the temperature was measured with a system of several thermocouples placed around the film.

CRYSTALLIZATION

The transparent film was mounted on the specimen table immediately after the crystals had melted and was left to come to room temperature. Scattering of the central beam was measured for two perpendicular positions corresponding

to the crossed and parallel directions of the Nicols. Hereafter, these orientations, will be called "crossed" and "parallel". Since crystallization at room temperature occurs very slowly, measurements were made twice daily to record changes of the scattering patterns; each pattern measurement took 10–15 minutes. In Figure 1, the variations of scattering diagrams with crossed Nicols with time is plotted on polar coordinates, and in Figure 2, with parallel Nicols. The figures show that at the outset of crystallization the plot of the scattering

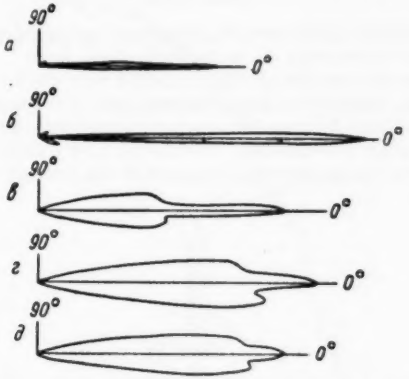

FIG. 1.—Variation of the scattering diagram taken with crossed Nichols as function of time. Days of crystallization: (letters at left of figure from top to bottom) *а*—first (magnif. 10 ×); *б*—second (magnif. 5 ×); *в*—third (magnif. 2 ×); *г*—fourth; *д*—twentieth (decreased 2 ×).

is strongly elongated in the forward direction. With crossed Nicols maxima appear on both sides; on polar coordinates they appear as small appendixes. During the crystallization process, they grow rapidly and often overlap into the forward part of the diagram with this forward part also growing, but at a slower rate. The size of these lateral maxima is equal in some cases and different in others, depending on the particular spot of the rubber film chosen for investigation. Uneven crystallization is the probable cause for this pheonomenon: some areas of strong crystallinity are formed while crystallinity is absent in others.

FIG. 2.—Variation of the scattering diagram (taken with parallel Nichols). *1, 3, 7*—Days of crystallization, starting from the day the film was melted.

The direction of the maxima is almost symmetrical with respect to the direction of the incident beam, forming a 4–6° angle with it. It is possible to decrease the divergence of the straight beam to 1° by using a narrower beam. During the crystallization process the scattering intensity increases greatly, for example with crossed Nicols by a factor of 15–20 in the foward direction. The scattering diagrams measured with parallel and crossed Nicols exhibit different shapes and change differently during the crystallization process. With crossed Nicols, the increase in crystalline phase appears clearly through the growing

lateral maxima. With thicker films, these peculiarities become less pronounced or disappear all together, in which case the plot of the scattering becomes an elongated ellipse. In comparing diagrams determined with different crystallizations rates, it can be shown that slower crystallization produces less elongated scattering patterns. This is in agreement with the general theory of light scattering and indicates the formation of smaller crystallites.

MELTING

Measurement of the light scattering diagrams during the melting process in a film showed that the crystals do not change their form. The shapes of the scattering patterns do not change until brought very close to the melting temperature; only the intensity of the scattered light is decreased. This may be seen clearly from Figure 3 where the diagrams measured with crossed Nicols are plotted on right angle coordinates. No matter how complicated the shape of the plot, it remains unchanged until the end of the melting. Ratios of the in-

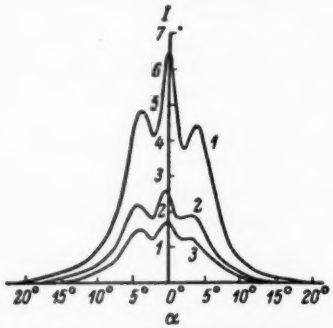

FIG. 3.—Variation of the scattering diagram taken with crossed Nicols as function of temperature. *1*—at 21°, *2*—at 54°, *3*—at 69°.

tensity of the central and lateral maxima at various temperatures are given in the table were they appear to be practically constant. This may be explained if one assumes that during the melting process the crystals do not vanish one by one, but rather that a gradual decrease of their anisotropic properties takes place due to the increased thermal molecular motion and that gradually the refractive index of the crystals approaches that of the amorphous phase. The processes of melting and crystallization in polymers are irreversible.

The observations with crossed Nicols show that the increase of the intensity of scattered light varies in different directions; therefore, the degree of crystallization cannot be determined by the increased scattering intensity in one arbitrarily chosen direction. It is necessary for that purpose to measure the complete angular distribution. During the melting process, however, the intensity of scattering measured in any direction, including the forward direction, will give an indication as to the degree to which the amorphous state has been reached or to what extent the crystals have melted. This last fact enables one to used scattering as a simple, convenient, and sensitive method for measuring the melting range of polymers and crystallites. If one places a thin crystallized nonoriented film between crossed Nicols and measures the intensity of the light

scattered in the forward direction, the intensity will decrease from the temperature where melting starts to the temperature where melting is complete and the film has become amorphous.

In thick films where multiple scattering takes place, the intensity of the depolarized component will increase in the initial stage of melting since the decreasing differential between the refractive indexes of the amorphous and

FIG. 4.—Variation of the intensity taken with crossed Nicols in the forward direction as function of temperature.

crystalline phases leads to decreased scattering, that is, to increased total intensity. On observing the melting of the neoprene film crystallized at room temperature, we found that with sufficiently slow heating, variation of intensity begins practically at the temperature of crystallization. The difference between the temperature of crystallization and the beginning of melting depends on the rate of heating and the sensitivity of measurement.

TABLE I

Plot (fig. 3)	Ratios of the central intensity to one of the lateral (side) maxima
1	1.3
2	1.2
3	1.2

The melting curve is obtained by plotting the intensity as function of the temperature, Figure 4; one can see here intermittent, slight maxima (the intensity is measured in galvanometer calibration units). This irregular thermal variation of the intensity may be due to changes in the microstructure of the crystals. The rate of heating was 3° per hour. Figure 4 shows that melting was completed at 45° for this sample. The temperature that corresponds to the completion of the melting depends on the temperature of crystallization and

probably on the quantity of the crystalline phase present. Figure 5 gives the melting curve of neoprene crystallized at 0°. In these curves even more pronounced irregularities appear than in the case of room temperature crystallized neoprene. At 4° a slight maximum appeared; its appearance is probably connected with increasingly favorable conditions for crystallization at that temperature. The melting process proceeds rapidly from 18–20° and is complete

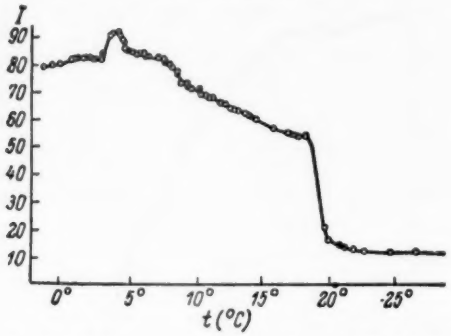

FIG. 5.—Melting curve of neoprene rubber, crystallized at 0°.

at 22°. The intensity increases at the outset of melting and may be explained by the fact that the film may not have been sufficiently thin. If one stops the melting process and begins cooling, a hysteresis phenomenon is observed since destruction of the crystalline phase occurs easier than its formation. If the melting process is performed slowly, Figure 6, Curve *1*, and subsequently one follows through with cooling, Figure 6, Curve *2*, and then continues melting

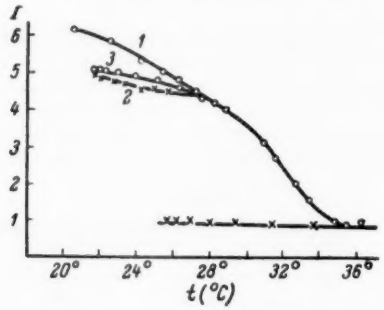

FIG. 6.—Formation of the hysteresis loop. 0–0–0—heating; x–x–x—cooling.

Figures 6, Curve *3*, the initial and final point of the loop are found to coincide. This means that the melting curve is an equilibrium curve. The slope of the hysteresis loop depends on the cooling rate and on the temperature at which the cooling was started. If the cooling is started at the temperature of complete fusion, the curve runs horizontally, since the crystalline phase is not being re-established.

DISCUSSION

One of the conclusions we can draw from this study of the crystallization process is that the slow crystallization of neoprene is caused not by the slow growth of crystals but by the low probability of nuclei formation. The shape of the scattering diagram measured at the start of the crystallization with parallel and crossed Nicols indicates that the crystals are large. This means that the appearance of a few large crystals is characteristic for the initial stage of the crystallization and not the formation of a large number of small crystals as might be expected; these develop at a later stage. We made an attempt to determine crystal size from the angular variation of light intensity. It was assumed that the particles were isotropic and the formula for the first approximation for spherical particles was applied; the dielectric properties of the particles are assumed to be close to that of the surrounding medium[4].

We were convinced that the shape of the scattering diagram cannot be a function of the particle radii alone: the size of particles calculated from data obtained with small scattering angles (0–4°) was 2.5 times larger than that calculated from larger scattering angles. According to our calculations the radii of crystallites at the initial stage of crystallization are close to 5 μ; the calculation is possible at that stage with adequate accuracy when small scattering angles are used. Toward the later stage of crystallization, crystal size calculated from data obtained with small angle scattering remains the same, but the radius calculated from larger scattering angles decreased to 1.5 μ. The decrease in the size of the crystallites may be caused by hindered growth due to appearance of neighboring crystallites and to the decrease of amorphous phase available for crystallization. We also determined the size of the crystallites by microphotography of the neoprene film and found the mean linear size to be of the order of 2 μ. Thus it can be seen that the particle size calculated by the integro-differential equation that was proposed by Shifrin[4,5] is in good agreement with the experimental findings. It should be noted that the calculations carried out by Kean and Stein[2] for polyethylene on the basis of the Debye theory give a measure of uniformity which is not in accordance with the real size of the spherulites. Results based on the Debye theory concerning the heterogeneity of the system are affected by the size and internal fine structure of the spherulites and the space between them. An important result is the fact that the scattering diagram remains unchanged during the melting process; also important is the decrease of the lateral side maxima, the increase of which characterize the growth of the crystalline phase. It is concluded that during melting a qualitative change of the crystalline lattice occurs rather than a quantitative variation; this change occurs in all crystallites simultaneously. We think that this result is important for the understanding of the melting process. The hysteresis phenomenon and the presence of steps in the melting curve are indications of the process that takes place inside the crystals, but not of the melting and recrystallization of the crystallites as a whole.

The preservation of the shape of the scattering diagram confirms the correctness of the scattering theory. This theory refers to particles with little difference in dielectric properties and predicts that as a first approximation the shape of the plot should be independent of the refractive index.

In conclusion, it should be pointed out that the process of crystallization and melting when studied by the light scattering of neoprene conforms with the picture obtained by studies of other polymers through the polarized microscope. For example, it is easy to observe the initial stage of crystallization of

polyethylene; it consists of the instantaneous formation of single large spherulites. During melting, a decrease in double refraction takes place but the borders between spherulites remain sharp and do not change their positions. The initial and final stages of melting are difficult to study under the microscope; however, it can be shown that microphotographs of crystalline polyethylene before melting and after a short melting period are almost indistinguishable. The crystallization process of many polymers is not suited for microscopic observation. For neoprene the initial stage of crystallization completely escapes observation due to the low probability of nuclei formation. The melting in this case is, as for polyethylene, accompanied by a decrease of anisotropy in the crystals. There is, of course, much interest in investigating the light scattering in the crystalline polymer, i.e., the scattering from anisotropic particles which we will investigate in the future.

SUMMARY

The process of formation and melting of neoprene crystallites was investigated by the polarized light scattering method. Conclusions about the nonreversibility of the crystallization and melting processes were drawn on the basis of angular distribution measurements of depolarized and polarized components of light scattered from polymer films.

The appearance of a relatively small number of large crystallites is characteristic for the initiation of crystallization; further development of crystallization is accompanied by a decrease in the size of the crystallites.

All crystallites disappear simultaneously during the melting process. The size of the crystallites determined by microphotography corresponds approximately to the particle size determined by the formula for isotropic, spherical particles.

A method for the determination of the melting range of crystalline polymers is proposed.

ACKNOWLEDGMENT

We wish to express our gratitude to E. I. Sharakhova who helped with the measurements and to K. S. Shifrin for his valuable advice.

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THE ABRASION OF VULCANIZED RUBBER AGAINST WIRE GAUZE *

S. B. RATNER

SCIENTIFIC RESEARCH INSTITUTE OF THE PLASTICS INDUSTRY

V. E. GUL

LOMONOSOV MOSCOW INSTITUTE OF FINE CHEMICAL TECHNOLOGY

AND

G. S. KLITENICK

SVERDLOVSK RUBBER GOODS PLANT (USSR)

INTRODUCTION

Two parameters are characteristic for the abrasion of vulcanized rubber: the first is a decrease of bulk M and the second is a distance γ between peaks formed in the process of abrasion on the vulcanized rubber surface. According to Schallamach[1] the relation between these parameters is given by the following equations:

$$M = \text{const}\,\frac{P}{E} \tag{1}$$

$$\gamma = \text{const}\left(\frac{P}{E}\right)^{\frac{1}{2}} \tag{2}$$

$$M = \text{const}\,\gamma^3 \tag{3}$$

where P is the nominal specific pressure and E is the Young's modulus for rubber[2].

The Schallamach theory is based on the study of scratching vulcanized rubber with a blunt needle. Schallamach checked his theory by abrading vulcanized rubber on sandpaper, thus confirming Equation (1) whose validity had been found earlier[3,4].

However, there is an essential difference in the mechanisms of rubber abrasion with sandpaper or with a blunt needle. In the first case a gash occurs in the upper layer of vulcanized rubber, facilitating further abrasion, whilst treatment with a blunt needle produces deformation of rubber. It is of interest therefore to establish the laws[1–3] governing the abrasion of vulcanized rubber by a surface causing deformation of rubber without gashing. Such an abrasive is a wire gauze, which can be conceived as a system of blunt needles, particularly if the wear of rubber is due to friction against meshes of the gauze.

EXPERIMENTAL

Tests were made on rubbers of similar composition; their properties were changed over a wide range either through changing the nitrile content in buta-

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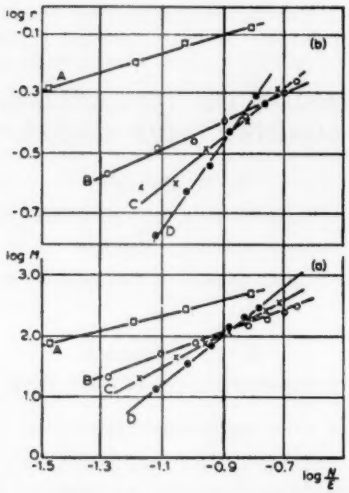

FIG. 1.—Relation of wear (a) and distance between peaks (b) versus deformation for vulcanized rubbers of different polarity. A is vulcanized rubber on an SKB base; E =30 kg/cm²; B is SKN-18; E =37; C is SKN-28; E =45; D is SKN-36; E =50.

diene-nitrile rubber (B, C, D) or by means of swelling of the rubber in dibutylphthalate or by varying the loading of the rubber. The types of rubber selected made it possible to vary over a wide range the character and intensity of intermolecular interaction, the structure characteristics remaining unchanged. The physical properties of these rubbers were investigated in detail[5,6].

Butadiene rubber (SKB) (A) was selected as a prototype of a rubber having minimum polarity though it also markedly differs from butadiene-nitrile (SKN) by the ratio of its 1,2- to 1,4-diene structural unit.

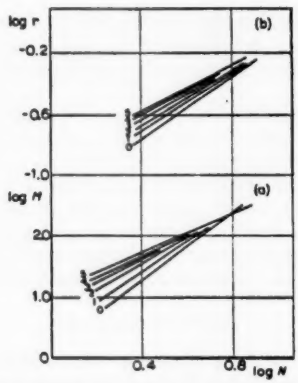

FIG. 2.—Relation of wear (a) and distance between peaks (b) versus the load for vulcanized rubber B with different degrees of swelling. (Figures by the straight lines correspond to percentage of swelling.)

Abrasion was studied on a Grasselli apparatus. Steel gauze with meshes 1×1 mm^2 in size and 0.25 mm wire thickness served as an abrasive surface.

By the application of gauze, swollen vulcanized rubbers can be studied. This is impossible in the case of abrasion with sandpaper, since the latter becomes clogged and its abrasive properties are thus altered. As can be seen from Figures 1 and 2

$$M = \text{const } N^{\alpha} \tag{4}$$

$$\gamma = \text{const } N^{\beta} \tag{5}$$

where N is the total normal load.

The values α and β, determined as slope tangents of corresponding straight lines, show that contrary to Schallamach's theory $\alpha \neq 1$ and $\beta \neq \frac{1}{2}$; thus α attains a value of 4 (and even of 6 for very hard rubbers).

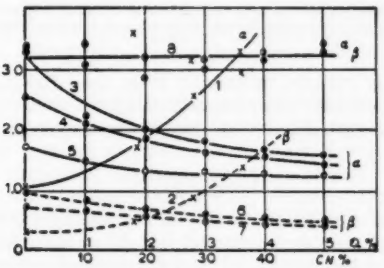

FIG. 3.—Variation in the exponent α (——) and β (- - - -) on changing of rubber polarity (*1–2*) and of the degree of swelling (*3–7*); the relation α/β is given on the straight line *8*. Lower scale on the X-axis: the increase in polarity with % CN, upper scale: % swelling Q.

RESULTS

A definite relation is characteristic for the changing of α and β (Figure 3). Both values decrease with decreasing polarity of a vulcanized rubber (when changing from vulcanized rubber D, made of SKN-36 rubber, to vulcanized rubber A, on an SKB rubber base), i.e., with weakening of the intermolecular interaction, particularly for non-polar vulcanized rubber A, where α and β are close to theoretical values (Curves *1* and *2*, Figure 3).

Moreover, analogous results were observed on swelling (Figures 2 and 3), since an increase of the ratio of swelling also leads to a weakening of intermolecular interaction. It should be pointed out that the data quoted above cannot be considered as a definite estimate of intermolecular interaction. The decrease of polarity or the increase in the degree of swelling is known to be followed by a decrease in modulus of the vulcanized rubber.

Consequently, experiments were made on rubbers loaded with different amounts of carbon black (and other types of carbons), increasing the hardness of vulcanized rubber; intermolecular interaction cannot be increased, however, owing to poor adhesiveness of the loading material. It can be seen from Figure 4 that α does not depend on loading, though the modulus of vulcanized rubber is changed by a factor of three. A similar phenomenon may be observed on changing the curing time (Figure 5). Thus α depends on the strength of molecular interaction, but not on the deformation of the rubber. Increase of the

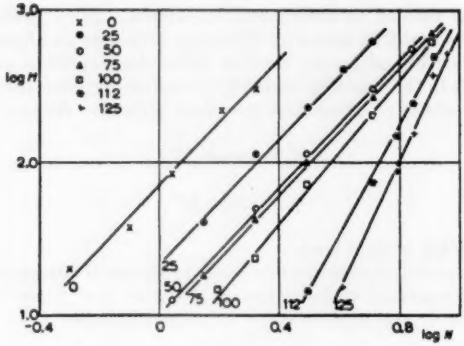

FIG. 4.—The effect of loading on the wear of vulcanized rubber B containing different amounts of thermal carbon black. Figures by straight lines show the amount of weight parts of carbon black per 100 parts of rubber.

slope of the angle for rubbers containing more than 100 parts (by weight) of carbon black is due to the specific macrostructure of the vulcanizate, the amount of rubber becoming insufficient for enveloping the excess of carbon black particles.

DISCUSSION

In spite of the fact that values of α and β greatly differ from theoretical ones, their ratio is $\alpha/\beta = 3$ (Figure 2, straight line *8*), in accordance with Equation (3). But since $\alpha \neq 1$ the relation of wear resistance for comparable vulcanized rubbers may be reversed on transition from small to high loadings (Figure 2). It can be seen still more distinctly, if wear is considered in relation to value N/E proportional to the degree of vulcanized rubber compression.

As can be seen from Figure 1, hard vulcanized rubbers are less abraded at low degrees of compression and more abraded at high degrees, as compared with soft rubbers. This is important from the standpoint of selecting vulcanized rubber for working conditions. The ratio of wear values for a given vulcanized rubber is maintained under different loads only if $\alpha = 1$. But usu-

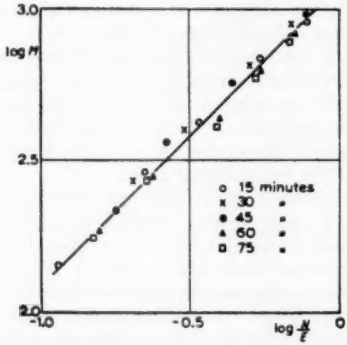

FIG. 5.—The effect of loading on the wear of neoprene with lamp black at different curing times.

ally the loads applied to vulcanized rubbers in laboratory tests differ from those under operating conditions; and further, these loads are varied in a very wide range during the work of the same type of article.

The problem of load differences in tests and in exploitation would have been of no importance if the characteristics of wear were invariant (independent of load). An invariant characteristic K for abrasion of vulcanized rubber against sandpaper was proposed[4]. It was called abrasion ratio $K = M/N$. On abrasion of vulcanized rubber against gauze in accordance with Equation (4), at $\alpha \neq 1$ the invariant constant will be expressed by ratio $M/N^{\alpha} = K_1$; this ratio may serve as a coefficient of the abrasion of vulcanized rubber for a general case.

TYPES OF WEAR

Comparison of results obtained during the abrasion of vulcanized rubber against gauze and sandpaper shows a characteristic difference between them: whereas a strong power function describes the abrasion against gauze, the dependence of abrasion of vulcanized rubber against sandpaper[1,3,4,8] upon load is almost linear ($\alpha \simeq 1$). This fact was also confirmed[8] for vulcanized rubbers A, B, C, D.

The difference in α values for gauze and sandpaper may be connected with the differences in the mechanism of abrasion of vulcanized rubber against these surfaces. Abrasion against sandpaper is connected with the penetration of abrasive grains into the upper layer of vulcanized rubber, followed by notching of this layer by the sharp edges of the grains. Later, notched surface particles are torn away. The abrasion of vulcanized rubber against gauze is connected with the indentation of a certain volume of vulcanized rubber into the cells of gauze, followed by stretching of this bulk and finally tearing off of pieces of the rubber. As deformation and tensile properties of vulcanized rubber greatly depend on its composition[6] (and on the degree of swelling) this may be connected with changing of α. It is interesting to note that α increases with increasing activity of the filler. Thus after introduction of 50 parts (by weight) of carbon black the value of α for rubber C, on changing from thermal carbon black to "lamp black", "furnace black", "spraying black", "channel black" will be 2.1, 2.3, 2.4, 2.7, 3.1, respectively.

Taking α as a criterion of the mechanism of vulcanized rubber wear, the following tentative classification may be proposed.

(a) "Cutting wear", which takes place owing to the notching of the vulcanized rubber surface. For example, treatment of vulcanized rubber on a lathe, wear at a roughly worked metal surface, as well as the undercutting of the wear groove in a rubber sleeve coupling with an angle[8]. Since this process practically amounts to pure cutting, the rate of wear will not depend on the load (but only on the rate of cutting tool movement), e.g., $\alpha \simeq 0$. This type of damage is, however, not "wear" in the conventional meaning of the word.

(b) "Abrasive wear" (against sandpaper, sand and gravel coverings). In this case, as was stated above, $\alpha \simeq 1$. This was checked for sandpaper[1,3,4,7].

(c) "Wear against gauze" and relatively smooth metal surface, where $\alpha > 1$. This was checked for gauze as shown above. This kind of wear is intermediate between (b) and (d).

(d) "Deformation wear" occurs owing to stretching and tearing of upper segments of vulcanized rubber surface, as a result of contact with a very smooth surface moving along the vulcanized rubber (glass, vulcanized rubber, polished

metal, etc.). In this case value α is expected to be very high and the smoother the surface the higher the value.

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RUPTURE OF RUBBER. V. CUT GROWTH IN NATURAL RUBBER VULCANIZATES *

A. G. THOMAS

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, WELWYN GARDEN CITY, HERTS., ENGLAND

1. INTRODUCTION

It has been noted in Part I of this series[1] (referred to hereafter as I), that if a nicked specimen of a natural rubber vulcanizate is slowly stretched, tearing occurs at the tip for quite small applied forces. In the initial stages, this tearing continues only as long as the deformation of the specimen is being increased, and virtually ceases if the deformation is held constant. This tearing is essentially time independent, and is termed "static" cut growth. If, however, the deformation is continued until the cut has grown by a few hundredths of a millimeter the growth becomes time dependent and catastrophic tearing takes place, the cut suddenly increasing in length by perhaps a millimeter or so.

If a nicked specimen is alternately stretched and relaxed to the unstrained state, the cut gradually grows even though the applied force is less than that required to produce catastrophic tearing. This phenomenon is termed "dynamic" cut growth.

This behavior can be compared to that of gum GR-S vulcanizates described in Part III[3], where static cut growth of the above type does not occur, a dead load on a test piece producing a more or less steady rate of cut growth.

In the present paper, measurements on natural rubber gum vulcanizates only are described, and the numerical results expressed in terms of the theory developed in previous papers (Parts I[1], II[2] and III[3]).

It has been shown in I and II that the tear behavior of differently shaped test pieces cut from thin sheets of thickness t may be correlated by means of the concept of the energy for tearing. This is defined as the value of $T\,[=(1/t)(\partial W/\partial c)_l]$ at the instant of tear, and is denoted by T_c. In the definition of T, is the total elastic energy stored in the test piece, c the length of the cut, and the subscript l indicates that the differentiation is to be carried out at constant displacement of those parts of the boundary that are not force-free. It was also shown that a convenient and direct method of obtaining T_c is by the use of the "simple extension" tear test piece described in I and shown in Figure 1, and this has been used for most of the experiments. Under most conditions, T for this test piece is nearly independent of the cut length, width of the test piece, and modulus of the rubber; T is very nearly equal to $2F/t$ where F is the force applied to the arms. In the cases where the use of the above approximate relation between T and F introduces an appreciable error, the exact theory given in I was used.

2. STATIC CUT GROWTH

A simple extension tear test piece was prepared with the tip of the cut formed by a razor blade, place in a tensometer, and the tip of the cut observed

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through a low power microscope. On extending the test piece it could be seen that tearing was occurring at the tip. The freshly torn surface could be distinguished from the original under suitable illumination by means of the slight angle they made with one another. The freshly torn surface appeared to be in the form of a shallow arrow-head. If the specimen was viewed in a direction perpendicular to the plane of the sheet, the appearance of the tip was somewhat as shown in Figure 2. This is reminiscent of the effect noted by Busse[4] when a cut is made in a sheet of highly stretched gum rubber, and suggests that this characteristic formation is due to the fact that at the tip the rubber is highly

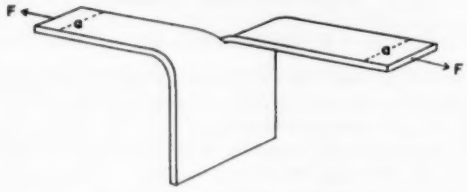

FIG. 1.—Simple extension tear test piece.

extended and thus crystalline and very hysteretic. That hysteresis plays an important part is suggested by the observation that, on relaxing the test piece, the characteristic formation disappeared when a sufficiently low strain was reached. On restretching, further cut growth took place at the new tip in a very similar manner to that which it would have followed if the whole incision had been made with a razor blade. A slight difference was noticeable, however, in that when cut growth occurred the initially smooth tip became somewhat rougher and on relaxing and restretching the new tip was not quite so well defined. This roughening, which continued with successive cycles, will be discussed later.

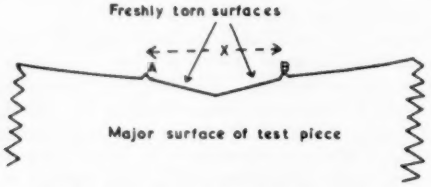

FIG. 2.—Tip of cut during static cut growth.

The amount of cut growth which has occurred on application of a given force can be estimated by measuring the width of the torn rubber at the tip, the distance AB ($= x$) of Figure 2. As the rubber just around the tip is presumably stretched to about its limiting extension ratio, λ_b, the distance the cut has grown, Δc, referred to the unstrained state, is given approximately by

$$\Delta c = x/2\lambda_b \qquad (2.1)$$

The measurement of x is facilitated by applying a small amount of a suitable powder, e.g., carbon black, to the inside of the tip of the cut before stretching takes place. If the tip is then viewed throughout its thickness as the test

TABLE I

Mix	λ_b	C_1, kg/cm²	C_2, kg/cm²
A	8.3	1.24	1.16
B	7.6	2.34	1.12

piece is extended, the freshly torn surface can be seen as a pale area in a dark surround and x estimated by an eyepiece scale in the microscope. The corresponding T values can be found from the applied force, F. In this way static cut-growth curves were obtained for rubbers A and B, prepared from the mixes in the Appendix.

Conventional tensile rupture tests were made to find λ_b, and also stress-strain measurements to determine the elastic constants C_1 and C_2 as described by Gumbrell, Mullins, and Rivlin[5]. Table I shows the results.

From Equation (2.1), Δc can be calculated, giving the cut growth curves shown in Figure 3.

It was found empirically that Δc was approximately proportional to T^2 except at the highest T values approaching T_c, where in any case Δc was becoming time dependent. Figure 4 shows the plot of Δc vs. T^2 for rubbers A and B. Assuming proportionality,

$$T^2 = G_s \Delta c \tag{2.2}$$

The values of the constant G_s were found to be 1.6 and 2.7×10^{16} c.g.s. units, respectively, for the two rubbers.

3. DYNAMIC CUT GROWTH

Experiments have been done with the simple extension tear test piece using the apparatus shown diagrammatically in Figure 5. This consists of a rocking arm A driven by a crank C; A carries a rod R, which can be slid along and

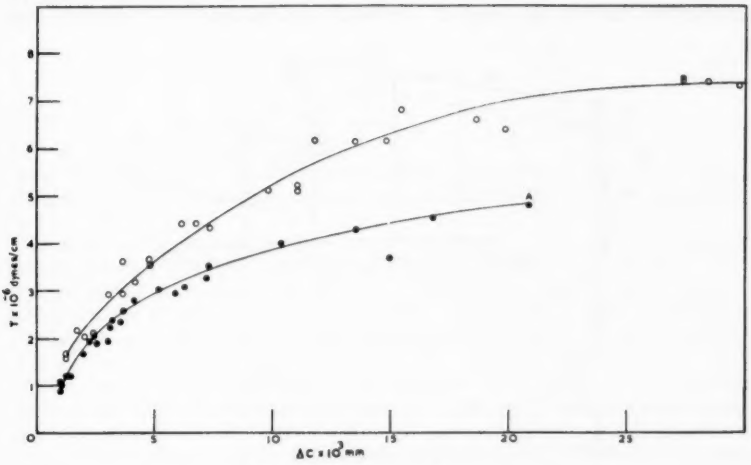

FIG. 3.—Static cut-growth curves.

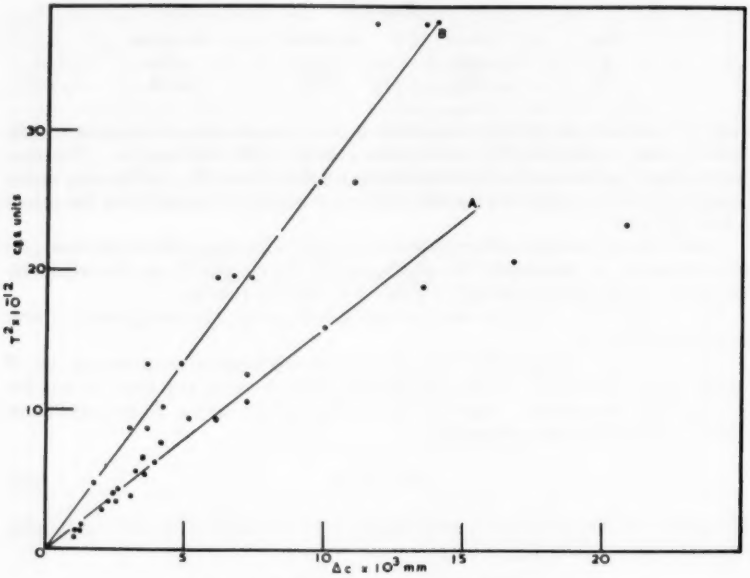

FIG. 4.—Plot of T^2 vs. Δc for static cut growth.

clamped where required. The test pieces *P*, usually four in number, are attached to this rod by means of calibrated spiral springs *S* and tension adjusters *B*, and clamped at their lower ends.

The amplitude of oscillation could be varied by moving the rod *R* and by altering the throw of the crank *C*. It was in general arranged so that the test

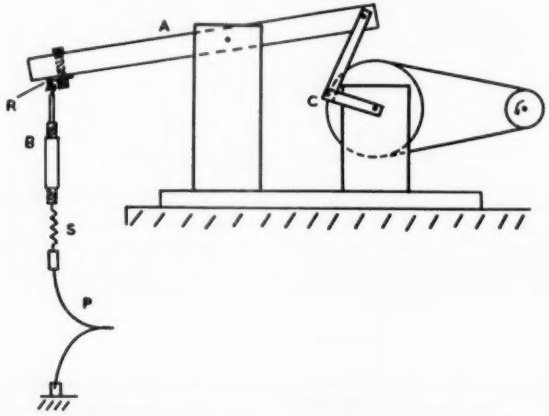

FIG. 5.—Dynamic cut-growth machine for simple extension tear test pieces.

pieces were completely relaxed for a portion of the cycle. The maximum forces were found from the maximum extensions of the springs. As cycling proceeded and the cuts grew, these maximum extensions of course decreased, but at intervals the springs were restored to their original maximum extensions by means of the tension adjusters. The amount of cut growth between successive adjustments was small (<1 mm), and the use of soft springs made errors from this source negligible compared with the spread in the results as a whole.

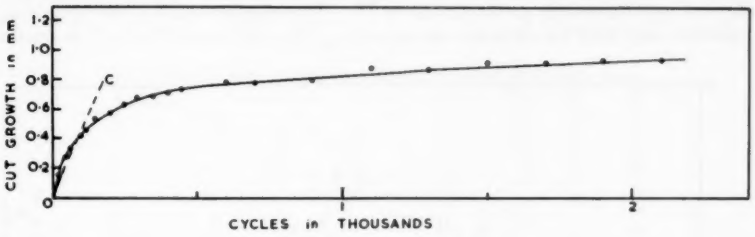

FIG. 6.—Dynamic cut-growth curve.

The cut growth was found by measuring with a microscope the distance of the tip from marks made on the test piece. The observation of the tip was made easier by slightly separating the arms and holding the test piece flat with a microscope slide.

The initial cut in the test pieces, which were 1–2 mm thick, was always formed by a razor blade. A typical cut-growth curve is shown in Figure 6 for the early stages of cut growth. Vulcanizate A was used and the maximum force was equivalent to a value of T of 1.96×10^6 dynes/cm. It can be seen that the initial rapid rate of cut growth gradually slows down and finally, after

TABLE II

Mix	C_1, kg/cm²	C_2, kg/cm²
C	1.46	1.20
D	1.58	1.24
E	1.70	1.31
F	1.80	1.36

a few thousand cycles, becomes substantially constant apart from irregular fluctuations. This decrease in rate is accompanied by a visible roughening of the tip of the cut.

It is of interest to compare the rate of cut growth which would be expected from the static cut-growth results for this rubber, assuming that the static cut-growth value of Δc occurs for each cycle. The broken straight line in Figure 6 gives the result, which is seen to correspond to a much faster rate of growth than the final value found in the dynamic measurements, but is consistent in order of magnitude with the initial rate found. The ratio of the initial to the final rate is about 10. The initial stage of the dynamic cut growth curve is not very reproducible, the cut attaining its final rate after very variable distances of travel.

In the subsequent experiments the dynamic rate of cut growth is taken to be that finally attained, when there is no further consistent decrease in the rate.

In practice, this means that the cut-growth curve for the first few thousand cycles is ignored in fitting the final slope to the line.

Experiments have been done on rubbers C, D, E, and F, with the results shown in Figure 7. The C_1 and C_2 values are given in Table II.

Figure 7 shows that the rates of cut growth of these rubbers are not significantly different. Rubbers D and E are nominally identical, except that D contains antioxidant.

In Section 2, it was found empirically that the amount of static cut growth Δc was approximately proportional to T^2. This suggests that a corresponding relation may hold for dynamic cut growth. The full line in Figure 7 is drawn

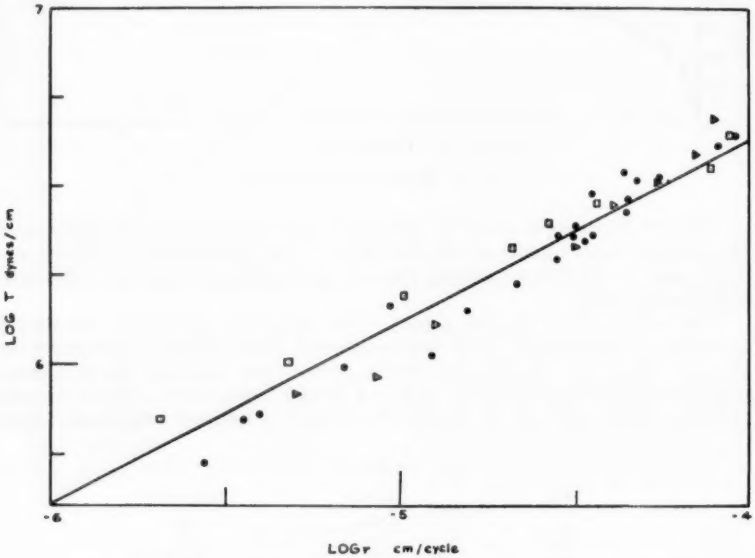

FIG. 7.—Relation between rate of cut growth and T for dynamic cut growth. Mix C (●); Mix D (⊡); Mix E (○); Mix F (△).

with a slope of 2, and it can be seen that it is consistent with the results except possibly at the highest values of T. Thus we have the relation

$$T^2 = G_d r \tag{3.1}$$

where r is the rate of cut growth in centimeters per cycle, and G_d a dynamic cut growth constant for these rubbers having the value 1.7×10^{17} c.g.s. units.

The cut growth per cycle is not very sensitive to the period of cycling at about the period used. No significant difference in rate was observed when the period was increased from 1.5 to 4.2 seconds, and the bulk of the measurements were carried out using the shorter period. The fastest speed of cycling which can be used with the present apparatus is limited by the oscillations of the test pieces and the attached clamps and springs.

4. VALIDITY OF THE RUPTURE CRITERION WHEN APPLIED TO CUT GROWTH

In I and II a theoretical treatment was given of two types of tear test piece, "simple extension" and "pure shear", on the basis of the criterion of rupture then proposed. It was shown experimentally in I that, for a given rubber, tearing occurred at the same value of T in test pieces of different shape, in particular the two above-mentioned types. In the case of cut growth it may be expected by analogy that equivalent values of T will similarly produce the same

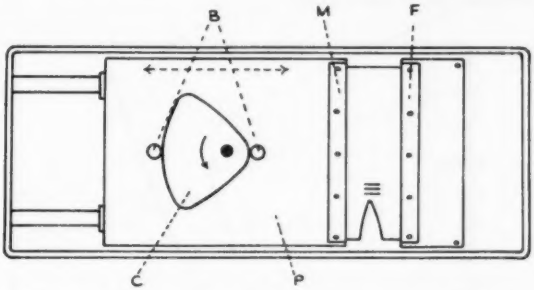

FIG. 8.—Dynamic cut growth machine for pure shear tear test pieces.

rate of cut growth. Experiments have been done to test this conclusion by comparing the behavior of the simple extension and pure shear test pieces.

The apparatus used to stretch and relax the pure shear test piece is shown diagrammatically in Figure 8. The cam C rotates, driving the platform P to and fro, maintaining contact continuously with the ball bearings B. A clamp M is attached to this moving platform opposite a similar fixed one F. These clamps are about 30 cm long and the test piece is stretched between them. The position of clamp F can be varied so that the test piece is unstrained for

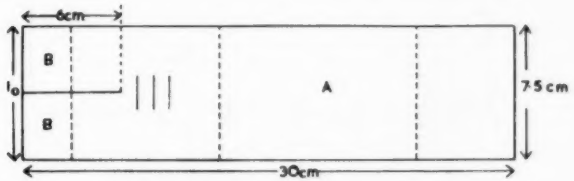

FIG. 9.—Pure shear tear test piece.

part of the cycle and is then stretched to a suitable maximum strain. The amplitude of motion of the clamp M is about 5 cm. As the test pieces used were thin (0.1 cm) compared with their length (6 cm), any buckling that occurred when the clamps approached each other produced only negligibly small strains. The period of cycling was 1.9 seconds.

The approximate dimensions of the test pieces, shown in Figure 9, were chosen so as to meet the requirements stated in I; viz., there was a region A substantially in pure shear and regions B which were substantially unstrained.

Two vulcanizates, A and B, were used. Their stress-strain properties in

pure shear were first determined by the method of Rivlin and Saunders[6]. The stored energy per unit volume E was then calculated as a function of the extension ratio λ_s by graphical integration under the stress-strain curve, giving Figure 10.

From I, T for this test piece is given by

$$T = El_0 \tag{4.1}$$

where l_0 is the unstrained length. The maximum value of λ_s was measured and hence, from Figure 10, E was found.

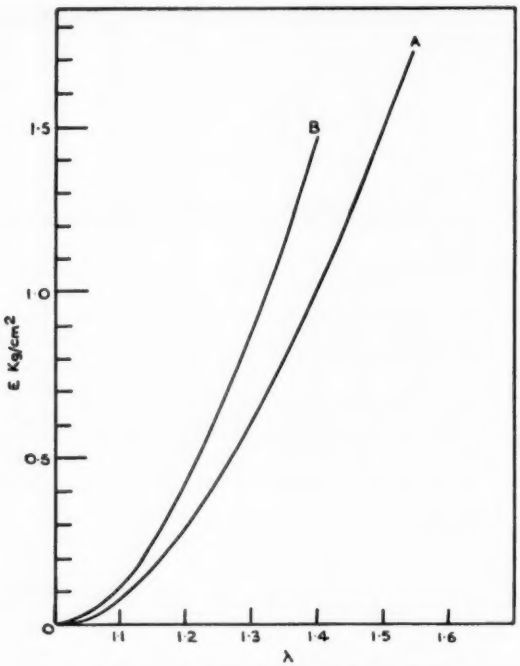

FIG. 10.—Stored energy/unit volume in pure shear.

Test pieces were cycled on the machine, and the distance of the tip of the cut from marks on the rubber, as indicated in Figure 9, was measured at intervals. After a conditioning period of a few thousand cycles the cut growth curve was substantially linear, as was also found with the simple extension test pieces. Figure 11 shows some typical results.

Simple extension tear test pieces were also tested as previously described. The range of the maximum values of T was about the same in the two sets of measurements; Figure 12 summarizes the results on both test pieces. There seems to be no significant difference in their behavior within the usual rather large spread in the results. Thus the rupture criterion proposed in I appears

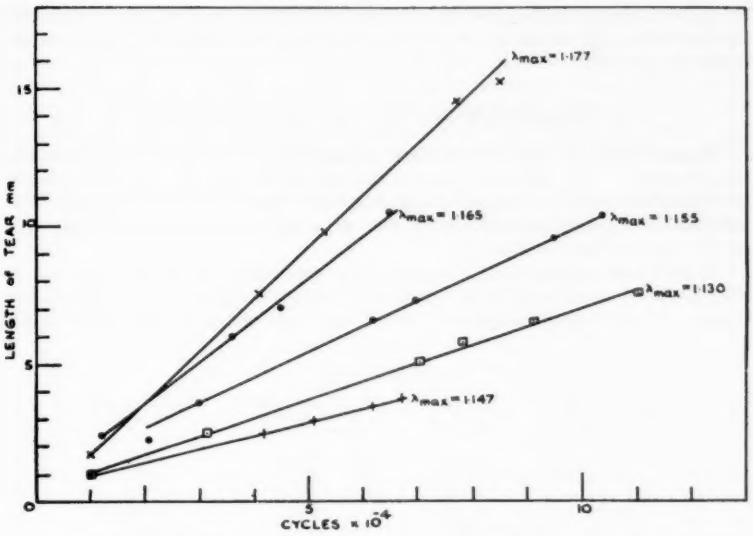

FIG. 11.—Dynamic cut-growth curves for pure shear tear test piece.

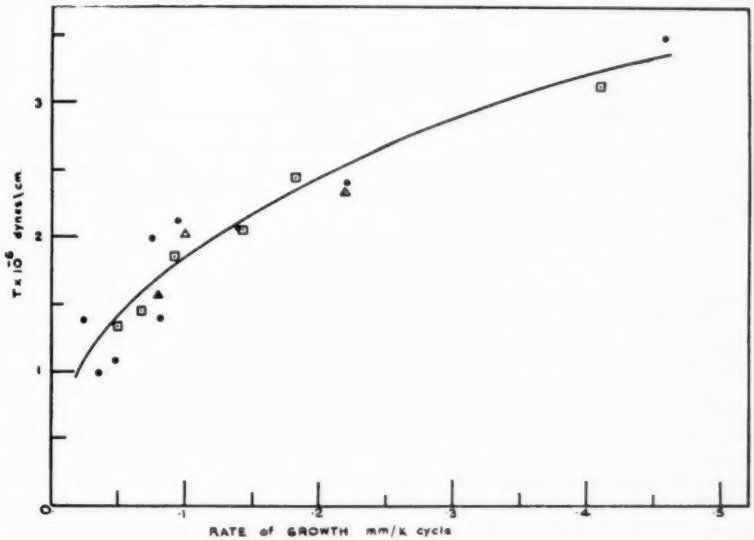

FIG. 12.—Comparison of rates of cut growth for simple extension and pure shear tear test pieces. Simple extension: Mix A (○); Mix B (●). Pure shear: Mix A (△); Mix B (⊡).

to apply to cut growth as well as catastrophic tearing, and in principle enables the rate of cut growth in one type of test piece to be calculated from measurements on another.

5. THE ROUGHNESS OF THE TIP OF THE CUT

It has been mentioned above that during cycling the tip becomes considerably rougher. The marked decrease in rate of the cut growth which is frequently observed in the initial stages of growth from a razor cut appears to be associated with the development of this roughness, so this phenomenon may be of considerable importance.

In II it was suggested that roughness or unevenness of the tip could act as if it produced a finite radius of curvature, making the strain concentration less acute. The observed roughness was of the same order of magnitude as the

TABLE III

T at which cycling took place $\times 10^{-6}$ dynes/cm	Rate of cut growth, mm/kc	T_c for cycled test pieces $\times 10^{-6}$ dynes/cm	T_c/E_b for cycled test pieces, cm
2.10	0.12	25.8	0.052
2.17	0.084	21.2	0.042
2.13	0.140	17.4	0.035
2.11	0.040	40.5	0.021
1.94	0.09	21.8	0.044
1.88	0.04	42.3	0.085
1.94	0.08	17.9	0.038
2.02	0.10	27.8	0.056
1.37	0.015	35.0	0.070
1.26	0.018	22.5	0.045
1.39	0.038	18.0	0.036
1.50	0.030	22.5	0.045
0.98	0.018	25.1	0.050
1.01	0.040	19.5	0.039
1.03	0.030	31.8	0.064
1.01	0.040	16.2	0.032

effective diameter d of the tip, the latter being deduced from the measured T_c value and the work to break per unit volume in simple extension E_b, using the relation

$$T_c \simeq d \times E_b \tag{5.1}$$

Equation (5.1) enables the effective diameter of the tip of a cycled test piece to be estimated from T_c, calculated from the force required to tear it catastrophically, and E_b. Thus a quantitative measure of the roughening which occurs may be obtained.

Table III results gives obtained on cycled test pieces of vulcanizate B, for which E_b was 5.0×10^8 ergs/cc. For a test piece with its tip formed by a razor cut, T_c was 8.2×10^6 dynes/cm, which gives a value of d of 0.016 cm. Also shown are the average rates of cut growth after the conditioning period which the test pieces were giving when they were being cycled.

The values of T_c for the cycled test pieces are erratic, but the following points may be noted: (i) these values of T_c, and hence d, are on the average about three times larger than those of the uncycled (razor cut) test pieces; (ii) comparing test pieces cycled to similar maximum values of T, there is a

tendency for those test pieces which gave lower cut growth rates to give higher values of T_c. This last point is not invariably borne out, as might be expected in view of the unevenness of the cut growth curve and the difficulty of determining the rate of cut growth just before the removal of the test pieces for tearing. The values of T_c predict d to be of the order of 0.03 to 0.08 cm. This is consistent with the observed roughnesses, which are quite pronounced, and suggests that this aspect of tear behavior is governed by fairly large-scale effects.

Table IV shows results for vulcanizates D, E, and F. The values of T_c for the cycled test pieces are shown for various maximum values of T attached

TABLE IV

Mix	T, dynes/cm $\times 10^{-6}$	T_c, dynes/cm $\times 10^{-6}$ (cut formed by cycling at T)
D	0.70	23.28
	1.02	17.26
	1.54	19.61
	2.11	23.12
	2.48	21.05
	2.81	28.2
	3.53	32.4
	4.36	38.2
E	0.72	16.1
	2.32	20.7
	3.32	22.6
	4.15	24.1
F	0.82	10.9
	0.92	12.3
	1.29	17.8

during cycling. These results cover a wider range of T than those of Table III and, although again some readings are erratic, there is a general trend for T_c to increase with T.

6. DISCUSSION

It has been found that the amount of static cut growth Δc occurring at the tip of a razor cut in a test piece is given approximately by Equation (2.2)

$$T^2 = G_s \Delta c$$

where G_s is a constant. An analogous relation (3.1)

$$T^2 = G_d r$$

holds for dynamic cut growth, with r the amount of cut growth/cycle. This similarity in the dependence of the cut growth on T in the two cases suggests that the basic mechanism is identical. The constants G_s and G_d differ by a factor of about 10, and this appears to be associated with the different shape of the tip of the cut in the two cases. In the dynamic measurements the cut be-

came very rough, effectively increasing the radius of curvature and presumably reducing the stress concentration. This is also indicated by the increased value of T_c for a cycled specimen, equivalent to a two to fivefold increase in radius of curvature.

The ratios of the cut growth constants and the T_c values may be related by the following argument. If the roughened tip is assumed to consist of a number of small sharp tips, the value of T for one of these will be less than that for the tip as a whole by a factor of, say, α. The ratio of T_c for the cycled to that for the razor cut specimen will then be α. If cut growth takes place by the growth of one of these elementary sharp tips, then as the value of T is lower by the factor α, the rate of cut growth will be reduced by α^2 according to Equation (2.2), giving

$$\left[\frac{T_c\,[\text{cycled}]}{T_c\,[\text{razor cut}]}\right]^2 = \frac{G_d}{G_s} \tag{6.1}$$

The uncertainty of the experimental data prevents any precise check of (6.1); however, it was noted in Section 3 that G_d was about 10 times G_s, and in Section 5 that the ratio of the T_c values was about 3 so that (6.1) is at least consistent with the data.

The experiments comparing dynamic cut growth in pure shear and simple extension tear test pieces are consistent with the tear criterion proposed in I and II. This implies that the roughness developed at the tip of the cut is independent of the overall shape of the test piece.

The dynamic cut growth measurements described in this paper have all been carried out with the test piece returning to zero stress each cycle. Some preliminary measurements with a finite minimum stress indicate that the rate of cut growth is greatly reduced, in keeping with previous work on fatigue life[7]. This is consistent with the view that the static cut growth is governed by a structure developed in the crystalline rubber around the tip as the cut grows. If the test piece is relaxed to zero stress, this structure will disappear with the crystallization and further cut growth will occur on the next cycle. If not, some of this structure will remain and will reduce the amount of cut growth on the next cycle.

SYNOPSIS

Cut growth in natural rubber gum vulcanizates has been studied using both steady and repeated loading. The results have been expressed in terms of the concept of the energy for tearing that has been put forward previously. With cut growth under repeated loading the tip, initially smooth, becomes rough and the rate of growth simultaneously decreases markedly to a final steady value. Some consequences of this roughening have been discussed. Measurements of cut growth under repeated loading have also been made using two different types of test piece. A rupture criterion, which has been previously proposed, predicts a definite relationship between the behavior of the two test pieces, and this has been confirmed experimentally.

ACKNOWLEDGMENT

My thanks are due to Dr. A. N. Gent for supervising some of the experimental work.

APPENDIX

	A	B	C	D	E	F
Rubber (S.S.)	100	100	100	100	100	100
Sulfur	3	3	2.5	2.5	2.5	2.5
Zinc oxide	5	5	5	5	5	5
Mercaptobenzothiazole	0.5	0.5	—	—	—	—
D.P.G.	—	1.0	—	—	—	—
Santocure	—	—	0.4	0.6	0.6	0.8
Stearic acid	1	1	2	2	2	2
Antioxidant	1	1	—	1	—	—
Vulcanization time (minutes at 140° C)	45	6	30	30	30	30

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DISTRIBUTION OF SIDE FORCE AND SIDE SLIP IN THE CONTACT AREA OF THE PNEUMATIC TIRE *

D. H. COOPER

DUNLOP RESEARCH CENTER, BIRMINGHAM, ENGLAND

INTRODUCTION

The side forces on tires have in the past been studied and discussed in such considerable detail that it should suffice here merely to restate the use to which they are put. The side force is useful insofar as it enables one to keep a vehicle on a particular course, and, to do this, it may at the same time have to resist side wind and road crown. It may occassionally be modified by the presence of wheel camber.

In the first place a side force is produced by rolling a tire at a slip angle, that is, so that the plane of the tire is at an angle to its direction of motion. With most passenger car tires, the side force is made to increase with slip angle at such a rate that a comparatively large side force, equal to three fourths of the weight carried, can be obtained when the tire runs at a slip angle between 5° and 10°. Because the resultant side force acts, as a rule, behind the center line of the tire by a distance known as "the pneumatic trail", it produces a moment called the "self-aligning torque", which, in a vehicle, is normally transmitted back to the steering wheel. For the driver, "self-aligning torque" can be a valuable guide to the amount of cornering force that is being applied to the tires, and to the direction in which the wheels are steered[1].

Now, whereas a number of authors have described how side force and self-aligning torque vary with slip angle, vertical load, inflation pressure, size of tire and rim as well as with the condition of the road surface, this paper describes the front to rear distribution of the cornering force within the contact spot. The intensity of cornering force, in turn, explains the presence and magnitude of total cornering force, self-aligning torque, and trail.

Work on cornering force was published by us first in 1949[2,3] and more extensively during and after 1954[1,4–8]. It is now linking up with the work of Martin[9], Fromm[10], Schlippe[11], and Kraft[12] who between 1935 and 1941 published diagrams of the distribution of horizontal forces and movements in the contact spot of a tire rolling along a straight path and at a slip angle.

Since that date, however, we have demonstrated that, at small slip angles, even at 0.5°, the forces due to inward and outward movement, or shuffle, are unimportant in comparison with those due to cornering[5]. The relative insignificance of slip due to shuffle during rolling can also be seen from the absolute values of 0.2 cms or so—obtained by Kern[13]. Chiesa[14] has pointed out the large extent to which road vehicles employ cornering forces during a normal journey and Gough[4,5] has stated the overridingly important role played by cornering forces in causing treadwear.

* Reprinted from *Kautschuk und Gummi*, Vol. 11, No. 10, pages WT273–277, October, 1958.

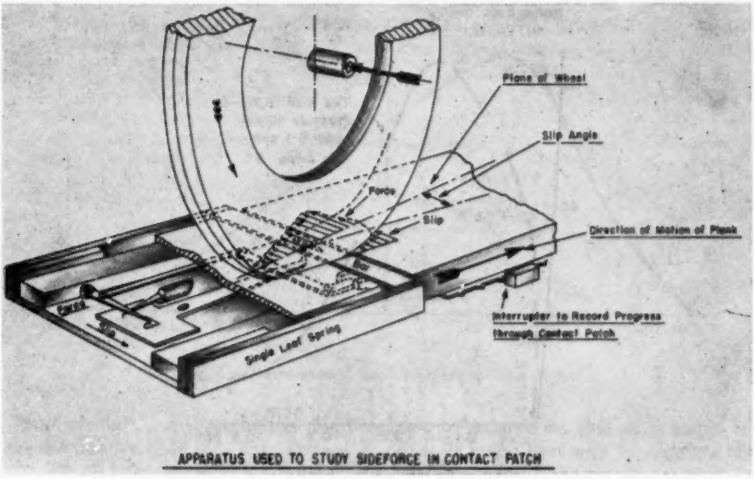

FIG. 1(a).—Sketch of apparatus used to study side force in contact spot.

THEORETICAL BACKGROUND

A theoretical study of the development of side force and camber thrust has been published by Fiala[15], and although we agree with much of what he states we do not agree with the assumption that

$$\frac{\text{Shear stress in contact spot}}{\text{Vertical pressure in contact patch}} = \text{constant}$$

because we believe we have established a more precise relationship between shear stress and vertical pressure. Nor do we agree with his assumption that the front portion of the contact spot is free from side-slip.

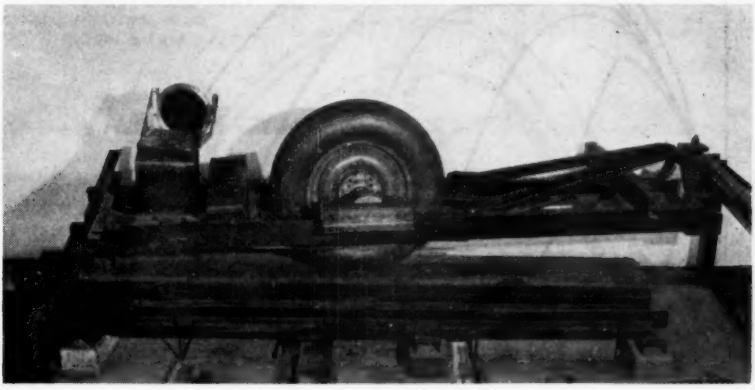

FIG. 1(b).—Photograph of apparatus.

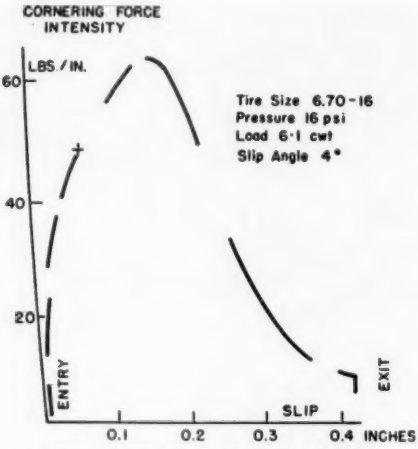

FIG. 2.—Cornering force intensity *vs.* side slip.

A paper on tire testing by Fonda[16] should also be mentioned, which, while contributing extensive data, does not offer much explanation of the development of side force. More pertinent, perhaps to our paper is his analysis of the sideway deflections of the tread in the contact area based on the theory of the

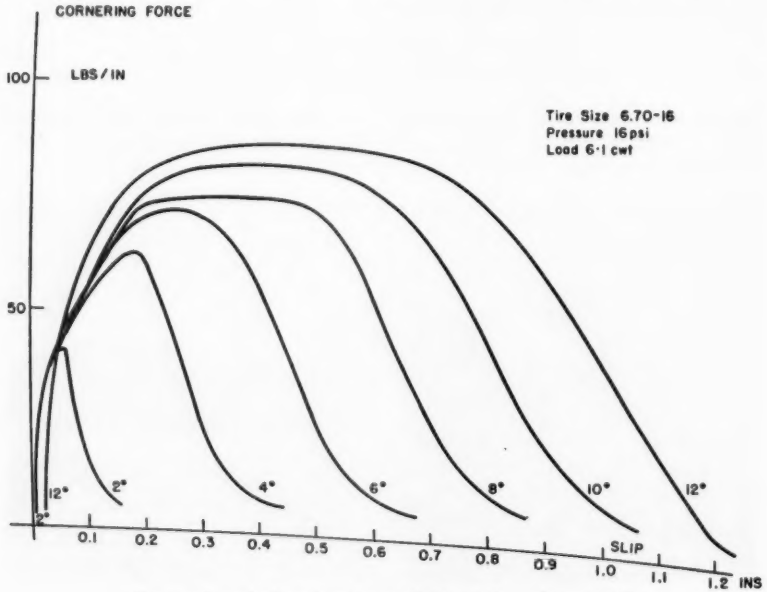

FIG. 3.—Cornering force intensity *vs.* side slip at slip angles up to 12°.

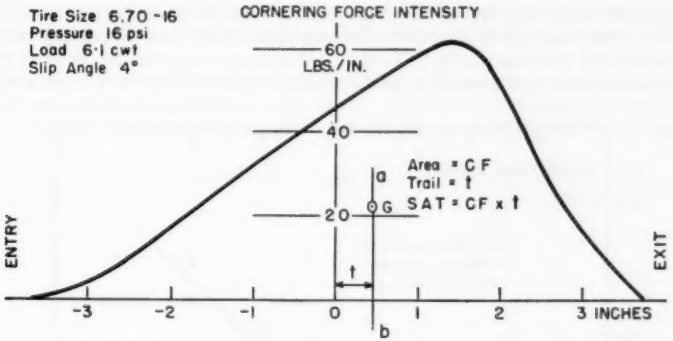

FIG. 4.—Cornering force intensity along the contact spot.

"taut string". Although it is not proposed to enlarge on this at present, we do not believe that the "taut string" hypothesis is the best way to simulate the conditions in a tire, and we hope to offer an alternative theory on another occasion.

THE CORNERING FORCE RIG AND TEST METHOD

Because we have already published a description of the cornering force rig[8], only a brief account is included here. The rig consists of a plank about 2.5 meters long and 28.7 cms wide, which is mounted on rollers so that it is free to run for a distance of 1.6 meters at 3 centimeters/sec (see Figure 1(a) and photograph 1(b)). Above the plank is a framework hinged at one end, in which there is an axle, wheel and tire; the tire is free to roll on the plank and may be

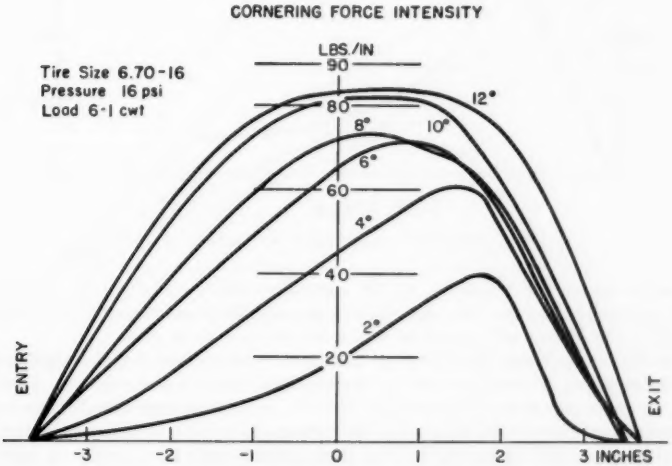

FIG. 5.—Cornering force intensity at slip angles up to 12°.

held at any slip angle up to 12°, by an adjustable stop at the free end of the frame. Near the end of the plank, the tire rolls over a bar, the emery-covered top surface of which is precisely level with the emery-covered top surface of the plank, and which is mounted on leaf springs, so that it deflects a small amount

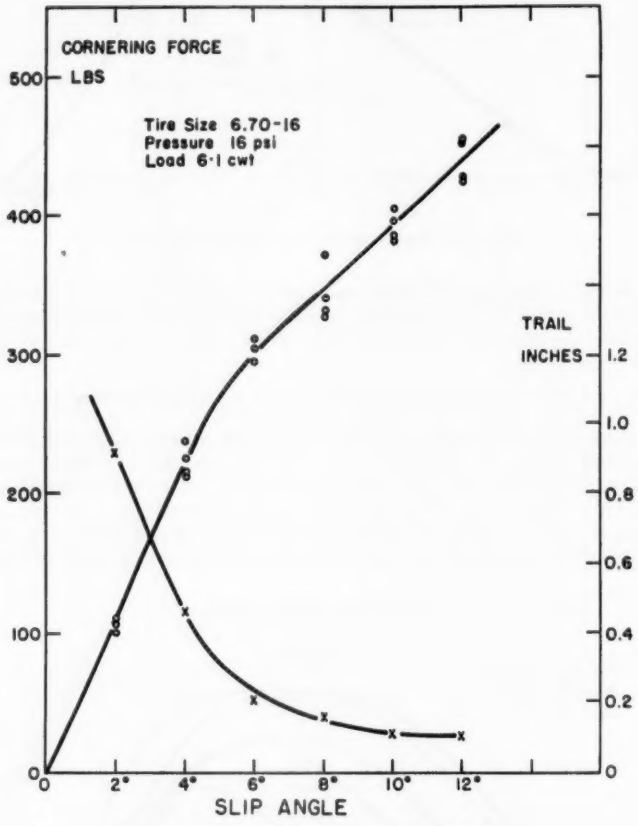

FIG. 6.—Cornering force and trail at slip angles up to 12°.

sideways under the influence of the cornering force. The spring cannot deflect vertically, but its sideways motion is magnified and transmitted through levers to the Y-axis of a graph which is drawn on a glass slide.

At the same time, the tread of the tire is penetrated by the upstanding prongs of a fork which is moved by an amount equal to the side slip. In this way, the side slip of the center rib of the tire, as it rolls over the fork, is transmitted to the glass slide, which, by its movement relative to the scribe records the side slip from front to rear of the contact patch. Finally, a contact breaker at the side of the plank is arranged so as to interrupt the tracing of the

slide at intervals corresponding to movements of 1 inch of the plank relative to the tire axle. Another device registers the position of the wheel center relative to the contact spot.

We have completed much preliminary work on this subject and have gained experience from testing about seventy tires. Very early, for example, we established that the sideways motion of all the ribs in the tread of a tire is nearly

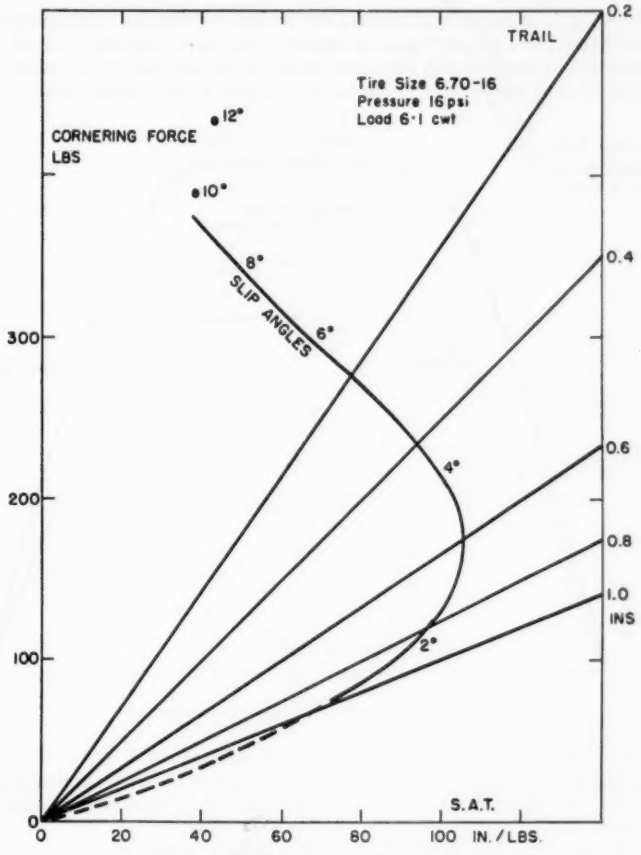

FIG. 7.—Cornering force *vs.* self-aligning torque.

equal when compared with the overall movement due to side slip and that, if so required, the cornering force can be made to rise to its full value before its measurement commences.

When the plank is drawn under the tire, a graph of cornering force intensity (lbs/in.) *vs.* side slip is drawn on a glass slide, Figure 2. The curve is interrupted at every inch of forward movement of the plank and two marks are

made on the slide in such a way as to fix the position of the wheel axle in relation to the beginning and end of the contact spot. A family of such curves for slip angles of 2°–12° is shown in Figure 3, in which each curve is the average of four results taken in four positions around the tire. This reduces any variability due to lack of uniformity which might occur in the tire.

EXPERIMENTAL RESULTS

Cornering force intensity at various slip angles.—From the original curve it is possible to derive a curve, Figure 4, of cornering force intensity (lbs/in.) *vs.* x, the distance, backwards and forwards, from the center line of the wheel. The rear half of such curves is a guide to the length of the contact spot. In this

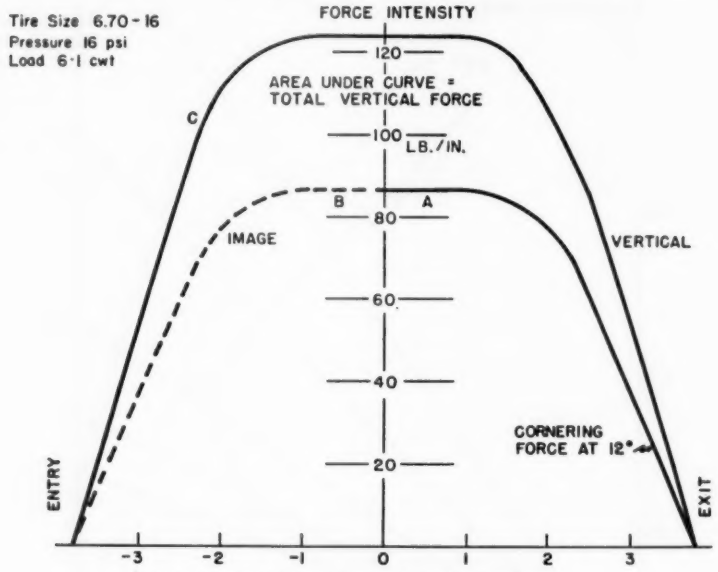

FIG. 8.—Vertical force intensity along the contact spot.

example, Figure 4, the length of the contact spot was $(3.7 \cdot 2) - 1$ or 6.4 in. It is necessary to subtract 1 inch, because the bar over which the tire rolls is 1 inch wide. The length of the contact spot measured from the contact print was 6.6 inches.

At 2° slip angle the cornering force intensity is distributed in an approximately triangular shape. It develops slowly and rises to a peak which is behind the center line of the wheel. At 4°, Figure 5, the force is larger but still triangular. At 6° and 8° the peak of the triangle is less sharp. At 10° and particularly at 12° there is a distinct flat plateau on the top of the figure, which is no longer a triangle but has become a trapezium. The appearance of the plateau signifies that the cornering force intensity can increase no further because the frictional force has reached its limiting value. The loss of cornering force intensity at the end of the contact spot is, of course, the result of the reduced vertical pressure in that region as the tread leaves the ground.

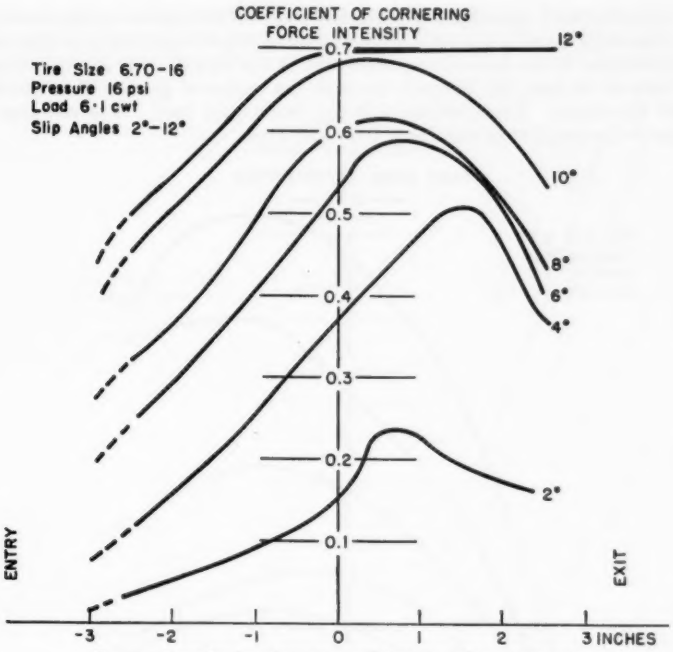

FIG. 9.—Cornering force intensity coefficient along the contact spot.

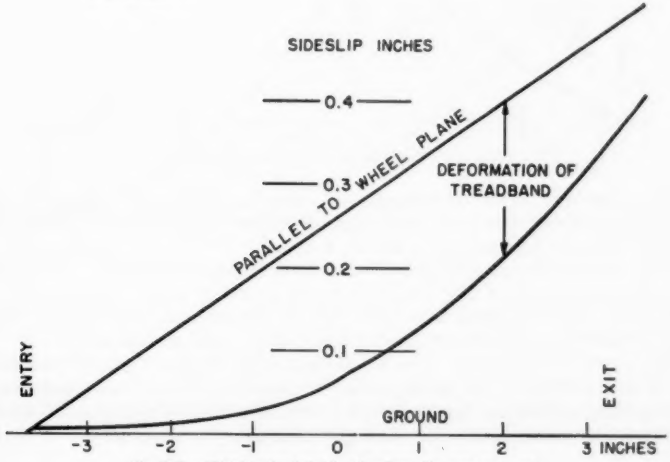

FIG. 10.—Distribution of side slip along the contact spot.

Cornering force, self-aligning torque and trail.—The area under the cornering force intensity curve is the total cornering force, Figure 4, and it is evident that at most times, it acts behind the center line of the wheel. The line of action of the force is, in fact, the line a–b through the center of gravity G of the area under the curve. The distance t is the pneumatic trail. The self-aligning torque is the product of cornering force and trail.

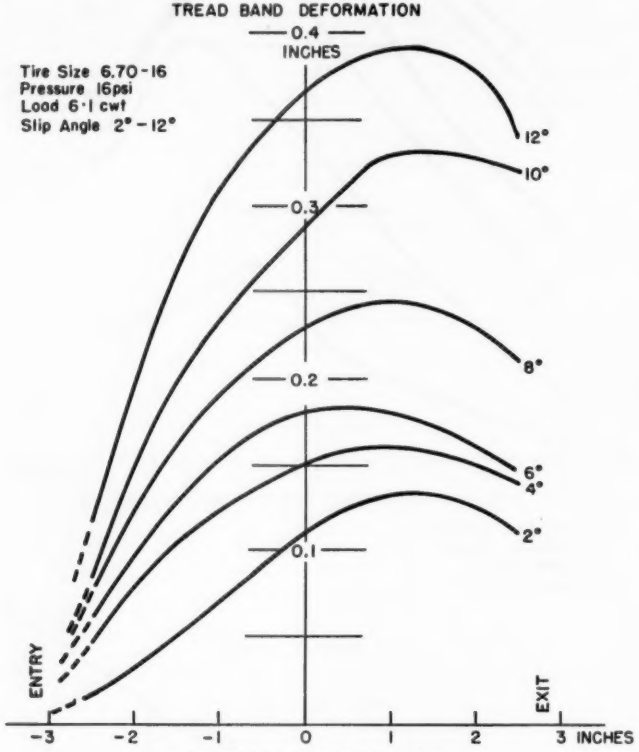

FIG. 11.—Tread distortion in the contact spot.

Slip angle and cornering properties.—The effect of the increasing slip angle on cornering force, trail, and self-aligning torque has been determined many times in the past by running a tire on a drum[1–4,7,8,15–17]. When the tire rolls on a flat surface the properties are, broadly speaking, the same[18]. The gradually changing shape of the cornering force intensity curve accounts for the slope in the total cornering force curve when plotted against slip angle, Figure 6, as well as the reduction of trail with slip angle, also in Figure 6.

The curve of cornering force *vs.* self-aligning torque, Figure 7, published first in Great Britain[1] and subsequently in Germany[4,17] is a convenient way of relating these quantities, together with pneumatic trail, on one graph. Riekert and Gauss have called this the "Gough" plot after the originator.

Vertical force distribution.—The distribution of vertical force over the contact area has been studied comparatively little; once by Martin[9], who drew the distribution of force along two fore and aft planes, once by Kraft[12] and once by Teller and Buchanan[19].

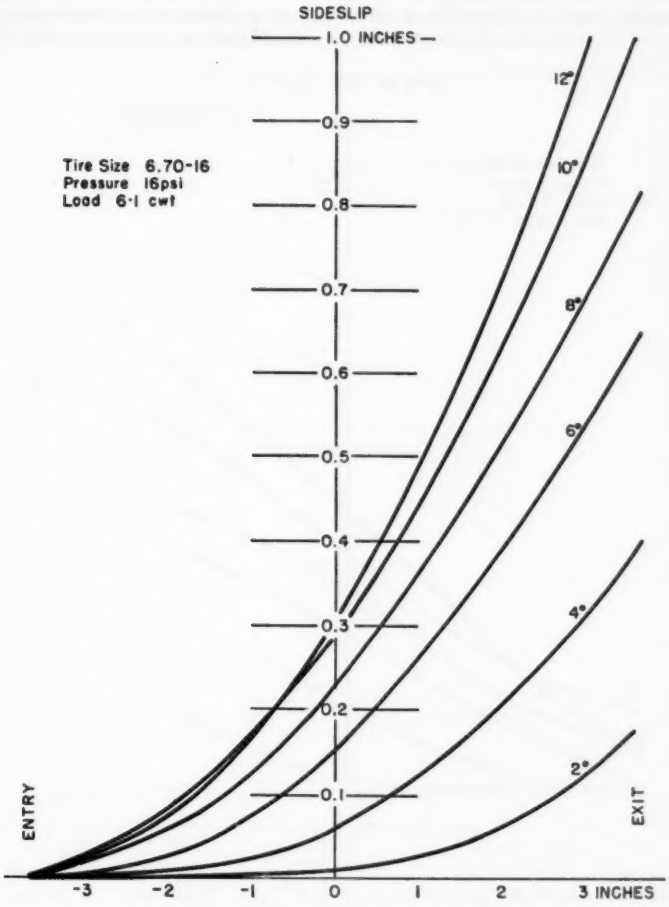

FIG. 12.—Distribution of side slip at slip angles up to 12°.

For our purpose, it is assumed that when the cornering force intensity for 12° slip angle reaches the plateau, Figure 5, the coefficient of friction is at its maximum value. And we have assumed that it remains at or near the maximum value and that the vertical force distribution has the same shape as the horizontal force distribution in the rear half of the contact patch, curve A, Figure 8. Believing that the pressure distribution is symmetrical, we have

first drawn the mirror image, B, of the horizontal force distribution, Figure 8, and then drawn a second curve C, with increased Y ordinates so that the area under the curve is equivalent to the vertical load on the tire.

The cornering force intensity coefficient, M.—*M* is the ratio of cornering force intensity at any point along the contact spot to the vertical force intensity at the same point. In Figure 9, a set of curves has been drawn expressing the values of *M*, the cornering force intensity coefficient, at each point from front

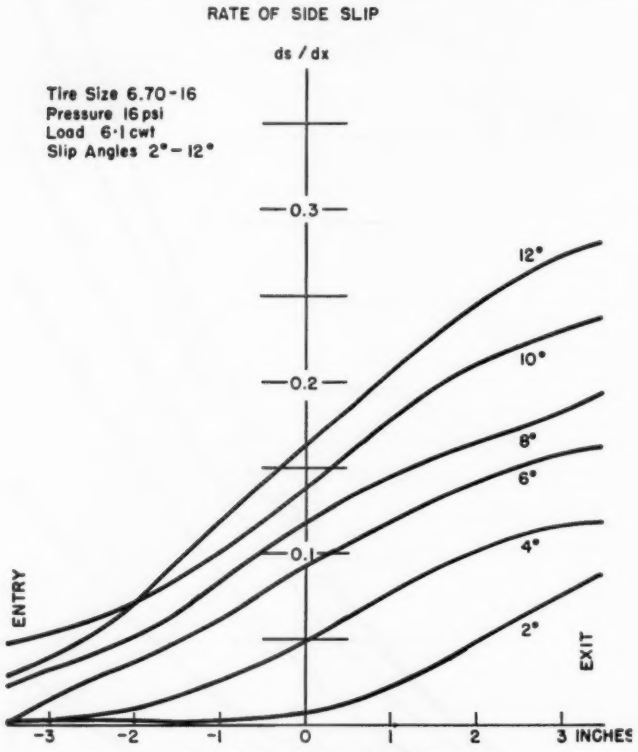

FIG. 13.—Distribution of d slip/dx.

to rear of the contact area over the wide range of slip angles available. It should be noted that the *M* values are not high. They would be higher if it were not for the fact that in the particular test illustrated here, the tire was purposely under inflated and under loaded.

Sideways distortion of the tread.—It is possible to derive from each one of the original curves in Figure 2, a curve of the distribution of side slip along the contact area, Figure 10. In this graph, the x axis indicates the direction of motion of the ground and the line is parallel to the plane of the wheel. At 4° slip angle, the tread at the start of the contact spot first follows the road for 4 inches or so and is then pulled towards the wheel plane by the elastic forces in

the tire. The distortion of the tread is worthy of further study and a family of curves of the distortion of this tread while it is in the contact area is given for slip angles up to 12°.

Side slip of the treadband.—From the family of curves showing the distribution of the side slip along the contact spot, it is interesting to note, first, that slipping increases from front to rear and that at slip angles above 8° the whole of the tread rubber is, in fact, sliding sideways over the ground.

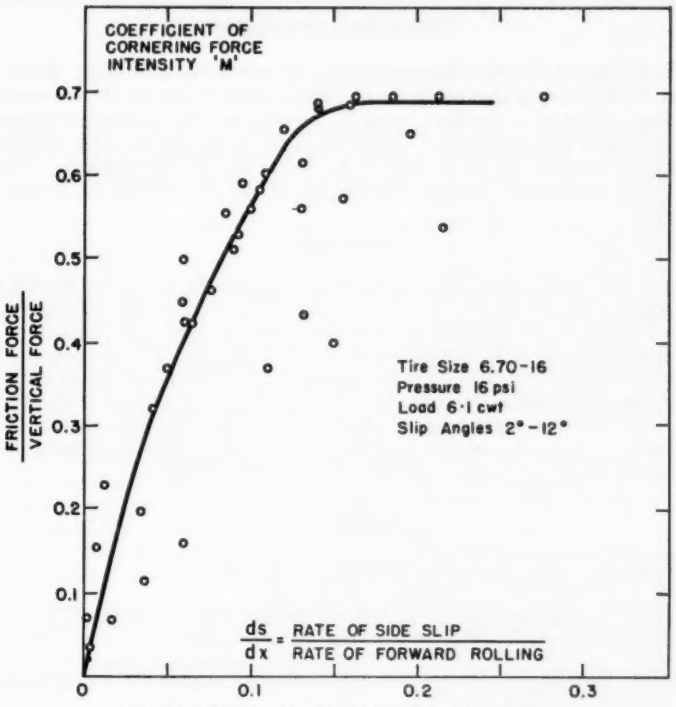

FIG. 14.—Cornering force intensity coefficient *vs.* d slip/dx.

Rate of slip curves.—If the wheel is moving forward at a uniform velocity v, in./sec, the distance x measured along the contact spot represents also the time $\frac{x}{v}$ secs and the slope of the slip curves is proportional to rate of sideways slip/rate of forward rolling motion.

$$\frac{ds}{dx} = \frac{ds}{dt} \cdot \frac{dt}{dx} = \frac{1}{v}\frac{ds}{dt} = \frac{\text{Rate of side slip}}{\text{Rate of forward motion of the axle}}$$

Curves of rate of slip with respect to distance moved through the contact spot are obtained by differentiating the slip curves and plotting ds/dx against x as in Figure 13.

Friction-rate of slip relationship.—Finally, in Figure 14, we have plotted cornering force intensity coefficient *vs.* $\frac{\text{Rate of side slip}}{\text{Rate of forward rolling}}$ and, allowing for experimental errors, have obtained one single curve.

Since cornering force intensity coefficient

$$= \frac{\text{Force of friction at any point}}{\text{Vertical force at same point}}$$

the curve shows how the force of friction is related to side slip. From this curve, it can be seen that the force of friction of any point in the contact area of a tire, rolling at a constant speed, is not constant but increases with rate of slip from zero to a maximum. After reaching its maximum value it remains constant. Only at speeds over 45 mi/hr does it begin to fall slightly. Finally this paper serves as a detailed illustration of the dissertation on friction by Gough[20].

SUMMARY

It is well known that, when a pneumatic tire is rolled over dry ground at a slip angle, a sideways force is developed. With the cornering force rig described here we are able to measure the front to rear distribution of the cornering force along the contact spot, the length of the contact area, the trail and the self-aligning torque. At the same time it is possible to derive the shape of the distorted tread and the front to rear distribution of side slip in the contact spot. By making certain assumptions concerning the distribution of the vertical force along the contact spot a relationship has been established between the forces of friction, rate of side slip and speed of rolling.

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INFLUENCE OF SURFACE CONDITION, DURATION OF MOLDING, PRESSURE AND TEMPERATURE UPON BOND STRENGTH BETWEEN COMPONENTS OF TIRE CASINGS*

V. A. Pinegin, S. A. Vasil'eva, and L. M. Kepersha

High bond strength between components of tire casings made entirely of synthetic rubber is one of the principal factors in service quality. The question of the bond strength between components of articles cannot be divorced from that of the tackiness of compounded stocks. This is of decisive importance in the process of manufacture of the components and in the building operation.

In work by the Chemical & Technology Department of the Nauchno-Issled. Inst. Shinnoĭ Prom. (Tire Research Institute) it was shown that the application of a bonding agent of natural rubber to components which are being plied up leads to a sharp reduction in the bond strength between them in the finished casing. In addition, this way of enhancing tackiness greatly complicates the technological process, adversely affects working conditions, and considerably increases cost. In spite of this, the industry was obliged to follow the procedure, as otherwise with present techniques and existing equipment it would be impossible to effect the building process.

Consequently, the elimination of a rubber based bonding agent from the process, by enhancing the tackiness of the raw rubbers and of compounded stocks, and also by rational use of various technological factors, is bound to be a fundamental line of development in improving bond strength.

Our work in seeking ways of enhancing bond strength between components of tire casings led us to study the influence of certain factors as follows:

1) the condition of the surfaces being plied up (the freshness of the surface, the time of standing, freshening by buffing, the methods of application of the bonding agent to the surfaces being plied up);
2) the pressure acting upon the contact area in the plying up of the raw blanks and in vulcanization;
3) the duration of the action of the molding forces in plying up;
4) the influence of the temperature of the surfaces being plied up.

All these factors were studied on testpieces of SKB, SKS-30 and SKS-30A vulcanizates, used for production of casings on an experimental basis.

The blanking out of the testpieces and their testing was carried out in the customary manner on existing apparatus. Nevertheless, instead of the usual closed-type mold used for vulcanization we used plunger-type molds. In Figure 1, we show the construction of molds of the closed and the plunger types.

The special feature of the plunger type is that the vulcanization of the testpiece can be carried out in strict relation to the external specific force which is applied; this force can be calculated easily and accurately for any desired vul-

* '*Prochnost' Svyazi . . .*'. 1954, p. 87–97). Translated by R. J. Moseley.

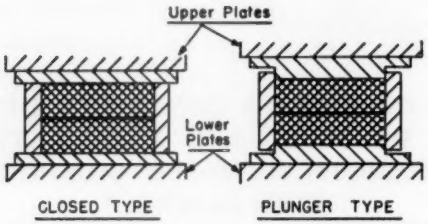

FIG. 1.—Vulcanization molds of two types; 1—closed type; 2—plunger type.

canization apparatus, something which cannot be done in vulcanization in molds of the closed type. This fact is very important in the study of the influence of factors upon bond strength between components which are being plied up.

CONDITION OF SURFACES BEING PLIED UP

The existing process provides for prolonged standing of the semifinished products and parts of casings. The times usually vary in the range of 3 to 24 hours, and sometimes are even longer. This is a result of the necessity of setting up intermediate stocks. Another opinion is that during the time of standing there takes place in rubber an equalizing out of the internal stresses which are set up during the processing of the rubber and in the manufacture of the components.

Working as we did after production line construction of casings had been established, we were obliged to examine the need for using varying standing times, i.e., their influence upon the quality of the tires.

It is generally known that prolonged standing of semifinished products and components greatly reduces tackiness. This is explained by the change in the condition of the surfaces being plied up, which takes place on account of:

a) oxidation of the surface layer by atomospheric oxygen;
b) copious blooming of the sulfur and other compounding ingredients, and also the deposit of factory dust;
c) geometrical alteration of the section of the surface.

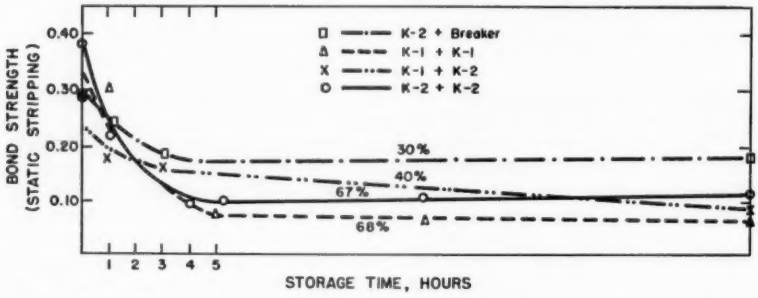

FIG. 2.—Bond strength (static stripping) of unvulcanized carcass rubbers as a function of the time of storage of the blanks prior to plying up.

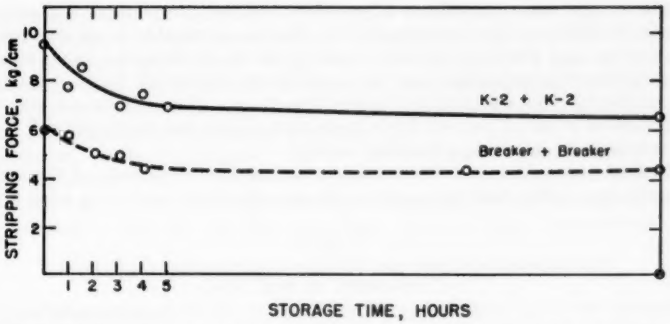

FIG. 3.—Bond strength (static stripping) between vulcanized rubbers as a function of the time of storage of the blanks prior to plying up.

Such alterations in the surface make it more difficult to ensure complete contact of the surfaces being plied up and do not give the necessary conditions for the diffusion process which is the basis of tackiness.

In Figure 2 we demonstrate the sharp falloff in bond strength in unvulcanized testpieces in rubberized cord as a function of the time of storage of the blanks prior to plying up. In the layers of cord rubberized with K-1, the most tacky rubber, the fall off on standing for 3 hours is 68% of the original value. At the boundary of the two rubbers, K-2 and breaker, this fall off is 30%. Between the layers of cord rubberized with one and the same stock, K-2, the fall off is 67%. At the boundary of the two rubbers K-1 and K-2 the loss in tackiness in 5 hours is 40%.

After 5 hours of storage of the blanks hardly any further loss in tackiness is observed.

In Figures 3 and 4 we show the alteration in bond strength between rubbers as a function of the time of storage of the raw blanks. The data once again show a fall off in bond strength in the first hours of storage.

There is a particularly marked fall off in bond strength between the breaker and tread in the stock based on SKS-30 and in the breaker and in the tread (dynamic testing).

It must be noted that carcass stocks based on SKS-30 hardly show any bonding capacity even with the minimum standing time of the rubberized cord. This is undoubtedly shown in the quality of the casings and in the productivity of tire builders.

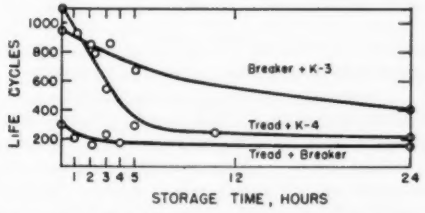

FIG. 4.—Bond strength (repeated shear) between vulcanized rubbers as a function of the time of storage of the blanks prior to plying up.

One of the main hindrances encountered in the production of high grade casings of 100% synthetic rubber is the absence of reliable bond strength between tread and breaker. In our work it was shown that the bond strength between these components may be considerably improved by freshening the surfaces being plied up, by fine ("velvet") buffing. However even under these conditions it is not at present found possible to apply the tread and roll it onto the carcass without using a bonding agent.

In this connection great importance attaches to the question of the method of application of the bonding agent to the surfaces which are being plied up.

TABLE I

DEPENDENCE OF DYNAMIC ENDURANCE UPON THE CONDITIONS OF TREATMENT OF THE TREAD

Treatment of the tread	Conditions of building of the specimen	Endurance under repeated compression of specimen with diagonally applied breaker layer, thousands of cycles
Untreated	Without bonding agent	223
	With bonding agent applied to a cold tread	182
	The same, on a hot tread	220
Buffed	Without bonding agent	255
	With bonding agent, applied to a cold tread	262
	The same, on a hot tread	277

We investigated the improvement of the existing method of applying bonding agent to the lower surface of the tread blank. The results showed that a bonding agent applied in a uniform and thin layer to the plying-up surfaces, with a temperature of the order of 50 to 70°, enhances the bond strength. This is explained by the fact that bonding agent applied to a cold tread dries slowly—the conditions of drying do not ensure complete evaporation of the solvent. In this case the drying of the bonding agent takes place from above, and this leads to the formation of a surface film which prevents the free evaporation of solvent from the lower portion of the layer of bonding agent.

TABLE II

BENCH TESTS OF CASINGS BEFORE AND AFTER RECONSTRUCTION OF THE TREAD PLANT

Method of applying bonding agent	Service life, km		
	Lowest	Highest	Average
On cold tread (unbuffed)	292	723	477
On hot tread (buffed)	505	1952	1013

The method we have developed for applying bonding agent to a hot tread in the tread apparatus has fully justified itself in industry.

In Table I we present data on the dynamic endurance of model specimens of a tread of SKS-30 and breaker of SKB as a function of the treatment of the tread and of the conditions of the application of bonding agent to it.

From Table I, but in the case of an unbuffed tread we get the best service life with specimens plied up without bonding agent. Specimens prepared by application of bonding agent to a hot surface of the tread are nearly as good.

Buffing of the tread enhances the service life of model specimens in compari-

son with specimens of untreated tread. The best service life in this case is with the specimens of buffed tread with bonding agent applied to the hot surface.

The recommended method of applying the bonding agent was adopted by the Moscow Tire Works and the tread plant was reconstructed on this basis. After reconstruction of the apparatus the service life of the covers in bench testing increased more than two-fold (Table II).

However, we do not consider the two-fold increase in service life to have been a consequence solely of this measure, since in the same period there were introduced by the works certain other organizational and technological measures, connected with the handling of casings entirely of synthetic rubber.

PRESSURE DURING BUILDING

The raising of the specific pressure during the plying up of raw specimens and of components of casings improves the bond strength between them.

This is explained above all by the fact that, other things being equal, a raised pressure ensures that a fuller contact is obtained between the surfaces which are being plied up, as a result of elastic or plastic definitions of the zones

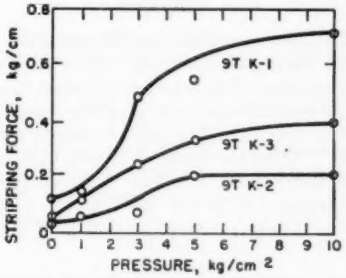

FIG. 5.—Bond strength (static stripping) of carcass rubbers as a function of the specific pressure during plying up.

with irregularities which are brought into contact during plying up. In principle we can explain by the very same circumstance the increase in the bond strength in the case of the application of raised specific pressures in the vulcanization of whole articles.

Nevertheless the raising of the bond strength is observed only up as far as definite values of pressure, the limit of which depends upon the polymer used and the composition of the compounded stock.

Our own investigations show that as the molding force is increased from 0 to 10 kg/cm² the bond strength in the unvulcanized specimens increases most sharply on the tacky rubbers (such as K-1), and not so sharply on the less tacky (such as K-2).

From Figure 5, it may be seen that the bond strength between rubbers in the unvulcanized state increases most intensely as the pressure is raised from 0 to 5 kg/cm²; the subsequent increase proceeds less intensely, and with K-2 it ceases almost completely. In Table III we show the bond strength of vulcanized rubbers as a function of the specific pressure in plying up.

From Table III we see that in the plying up of SKS-30 tread rubbers and SKB breaker rubbers the dynamic service life likewise increases as the specific pressure is increased from 0 to 100 kg/cm².

PRESSURE DURING VULCANIZATION

In the vulcanization of tire covers the most important factor, along with temperature, is the pressure.

The pressure of 22 to 25 kg/cm², which has been used for a long time by tire works was obviously established as the optimum for casings produced from natural rubber. For tire covers of synthetic rubber the optimum pressure should probably be some other.

TABLE III

BOND STRENGTH OF VULCANIZED RUBBERS (SKS TREAD, SKB BREAKER) AS A FUNCTION OF SPECIFIC PRESSURE DURING PLYING UP

Specific pressure during molding of specimen, kg/cm²	Number of cycles before failure	
	Repeated compression of specimens with breaker layer applied diagonally	Repeated shear of specimens with breaker applied vertically
0	$190 \cdot 10^3$	249
10	$2100 \cdot 10^3$	268
50	$3398 \cdot 10^3$	412
100	$4547 \cdot 10^3$	456

We investigated the influence of the specific pressure (varying in the range from 25 to 500 kg/cm²) during vulcanization upon the dynamic bond strength in laboratory model specimens of tread-breaker-tread type, and also in carcass specimens. In Figure 6 we show the curves for the dependence of bond strength upon specific pressure in vulcanization for laboratory specimens of the tread-breaker-protector type. From the figure it is seen that as the specific pressure is increased so is the dynamic bond strength in the specimens. The maximum value is reached at a pressure of 200 to 300 kg/cm². Further increase in the specific pressure leads to a perceptible reduction in strength.

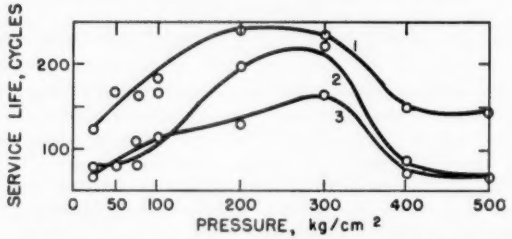

FIG. 6.—Influence of specific pressure during vulcanization upon the bond strength between tread and breaker in rubber specimens in repeated deformation: *1, 2, 3*—curves for three specimens with tread rubbers of different composition and with the same breaker composition.

The mix formula has a considerable influence upon the dynamic strength of the specimens; however in all our experiments with different combinations of formulas we always got an increase in the dynamic bond strength with increase in the pressure from 25 up to 200 to 300 kg/cm².

It is indicated in the literature that with increase in pressure there is an increase in the rate of vulcanization of the specimen which is under this pressure. Accordingly the fall off in bond strength at high specific pressures may be explained by over-vulcanization (reversion). For a full proof of this suggestion special investigations are however necessary.

In Figure 7 we show the dependence of dynamic bond strength in rubber-cord carcass specimens upon the specific pressure during vulcanization. As the pressure is increased, beginning at 25 kg/cm², dynamic strength increases and reaches its maximum at a pressure of about 200 kg/cm². Obviously with increase in pressure up to 200 kg/cm² the rubber stock penetrates into the cord threads to a greater depth, and because of this the bond strength of the fibers of the cord with the rubber increases.

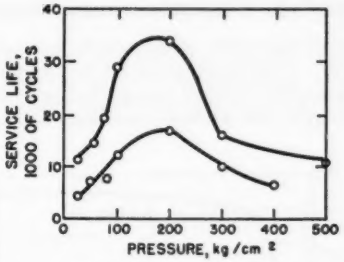

FIG. 7.—Influence of specific pressure during vulcanization upon bond strength in rubber cord carcass specimens in repeated deformation.

The dynamic strength of rubber cord specimens at pressure higher than 200 kg/cm² is reduced as in the case of the rubber specimens.

It was of interest to test what is the influence of the magnitude of the specific pressure during vulcanization upon the tensile strength of the cord. It is established by experiments that alteration of the pressure up to 500 kg/cm² has no essential influence upon the tensile strength of the cord threads—this remains practically constant.

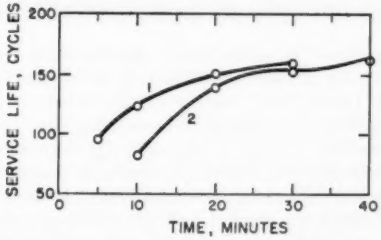

FIG. 8.—Service life of specimen as a function of the time of action of elevated pressure (50 kg/cm²) at the beginning of vulcanization: *1* and *2*—curves for two specimens, differing in composition of the tread and breaker rubbers.

We investigated also the influence of differing time of action of raised pressure in the vulcanization process. In the initial period of the process of vulcanization a pressure of 50 kg/cm² was applied; after a given interval of time this pressure was reduced to 20 kg/cm²; during this the pressure of vulcanization is reduced until the end. The time of action of the raised pressure of 50 kg/cm² was altered from 5 to 40 min.

From the resulting data (Figure 8) it may be seen that a raised specific pressure exerts the greatest effect in the initial period of vulcanization, up to

30 min (for a total time of vulcanization of the specimen of 100 min), after which this pressure may be reduced to 20 kg/cm² without noticeable adverse effect upon the bond strength.

The raised pressure is necessary only in the initial period, when the rubber is being softened and the vulcanization process is still taking place slowly. As vulcanization is accelerated so will the action of the pressure upon the bond strength show itself progressively less.

TIME UNDER PRESSURE DURING BUILDING

Increasing the time of the action of the specific pressuring during plying up raises the bond strength. This is explained above all by the fact that to attain complete contact between the surfaces being plied up a definite period of time is required, depending upon the surface conditions and on the force acting in this period.

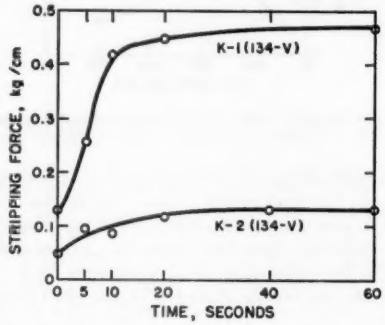

FIG. 9.—Dependence of bond strength between rubbers in the unvulcanized condition upon the time of action of the specific pressure (5 kg/cm²) during plying up.

By increasing the period of action of the specific force during plying up it is possible to compensate for inadequate force and, on the other hand, it is possible to reduce the time of plying up by increasing the force.

From Figure 9 it may be seen that increasing the time of action of the specific pressure upon the surfaces being plied up enhances the bond strength between them. However there is a limit to this increase and, as may be seen from the figure, with the rubbers in question after 5 to 10 seconds molding at a pressure of 5 kg/cm² the bond strength ceases to depend upon the time of plying up.

To obtain the best contact in plying up the rolling-on method is widely used. Increasing the number of passes is equivalent to increasing the time of action of the specific pressure in ordinary molding.

TEMPERATURE OF THE SURFACES

We investigated the influence of the temperature upon the bond strength between components which are being plied up in casings based on 100% synthetic rubber.

The results showed that raising the temperature of rubbers which are being plied up increases their bond strength. However there is a limit to the positive

influence of the temperature of heating; at temperatures which are too high we observe a reduction of bond strength between the components.

The increase in bond strength up to a certain limit during the heating of surfaces which are being plied up is explained mainly by the fact that the stocks in such a case become more plastic—this creates the conditions for obtaining full contact between the surfaces being plied up for lower specific pressure and shorter time of its action.

In Figure 10 we show the dependence of the bond strength between tread and breaker rubber upon the temperature of heating of the components being plied up.

In conformity with the casing building process being developed, we used heating prior to vulcanization for the tread stock only—the breaker stock had a temperature of 20°. In these conditions the tread was plied up with the breaker in the building process.

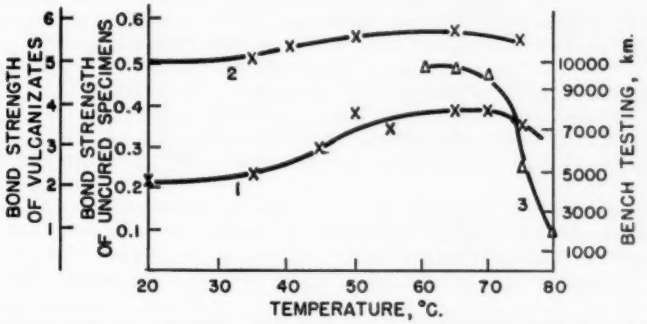

FIG. 10.—Bond strength as a function of the temperature of the surfaces being plied up. *1*—in unvulcanized specimens, *2*—in vulcanized specimens, *3*—in tire casings.

As may be seen from Figure 10, the bond strength in the unvulcanized specimens increases as the temperature is raised, up to 65 to 70°; the greatest increase is observed in the temperature range 35 to 60°. An analogous phenomenon is observed also for bond strength in vulcanizates even though in this case the dependence is less pronounced than with the unvulcanized specimens.

Bench testing gives good results for casings in which the temperature of the tread during building is from 60 to 70°. A higher temperature of the tread has a pronounced adverse effect upon the life of the tires.

CONCLUSIONS

As a result of the above experiments it is shown that the bond strength between components of casings where 100% synthetic rubber is used, may be significantly increased:

1) by maintaining the freshness of the surfaces being plied up by keeping standing to a minimum, by freshening the surfaces by fine ('velvet') buffing, and by applying a thin and uniform layer of bonding agent to the previously heated surfaces;

2) by increasing the specific molding pressure during plying up;
3) by increasing the specific pressure upon the constructions during vulcanization;
4) by increasing the duration of action of the specific molding pressure during plying up;
5) by raising the temperature of the components being plied up.

The rational exploitation of these points undoubtedly has an important effect and will ensure the improvement of the quality of the finished articles, particularly where 100% synthetic rubber is used.

ENHANCEMENT OF BOND STRENGTH IN TIRE CASINGS BY HEAT TREATMENT *

Kh. E. Malkina and A. P. Pukhov

Testpieces of carbon black stocks on a 100% synthetic rubber basis which do not adhere to surfaces may be satisfactorily bonded to each other if they are subjected to molding under a given pressure over a prolonged period. In this case the more plastic the stocks the greater the depth of their penetration into each other on molding, and consequently the higher the bond strength between the individual rubberized components. The best and most rapid joint is with components whose plasticity values are close to each other.

Carbon black stocks on a 100% synthetic rubber basis are highly thermoplastic. Thus preliminary heating of the blank components with subsequent molding ensures enhancement of the bond strength.

As a result of calendering, extruding, building and molding of the various types of component going into a tire casing stresses are set up between these components which tend to separate them and thus reduce the bond strength in the finished product. The removal of such stresses leads to enhancement of bond strength.

Since the mechanism of the removal of the stresses is a relaxation mechanism, the lowering of the stresses proceeds more rapidly and fully in heated blanks; thus the heating and maintenance of the heat of the heated raw casings, particularly before vulcanization, ought to lead to an improvement in their service properties.

These things are not usually disputed. Nevertheless until recently the quantitative side of the matter was not clear, i.e., whether it was possible by preliminary heating to increase significantly the serviceability of the casings (in particular on poor roads).

Suitable investigations were carried out in the technology division of the Nauchno-Issled. Inst. Shinnoĭ Prom. (Tire Research Inst.) to study this.

The method of enhancement of bond strength between components of tire casings by thermal treatment of the raw blanks before molding and vulcanization has the advantage that it is applicable in principle with all mix and impregnant formulas and the method makes it possible to reduce to a minimum or eliminate altogether adhesive dressings.

In order to ensure an effective improvement of the bond strength, we had first to develop suitable heating cycles. Thus, in developing cycles of preliminary heating for 100% synthetic rubber casings we investigated:

1) the enhancement of the plasticity of the stocks going into the casing as a result of the heating;
2) the conditions of scorching of the stocks on rapid heating and prolonged holding at high temperatures;
3) pore formation in stocks at high temperature;
4) the comparative value of the coefficients of volumetric expansion of vulcanization stocks going into the composition of the casings.

* Translated by R. J. Moseley from '*Prochnost' Svyazi. . .*', 1954, p. 158–163.

As a result of the work carried out the following [items 1) to 4)] were established.

1) The plasticity of carcass stocks used in casings begins to increase noticeably at 40 to 45°, and for tread stocks at 60°.

At 60° to 70° the plasticity of the tire stocks is a number of times higher than at 20°—for a tread stock 2.7 to 4 times as high, for breaker stock 4.5 to 7 times, for a carcass stock 4.5 to 9 times.

TABLE I

PERMISSIBLE TIME (MIN) OF HOLDING TIRE STOCKS AT VARIOUS TEMPERATURES

Stock \ Temp.	60°	80°	90°	100°
Tread	60–70	50	30	20
Breaker	55	50	30–40	30
Carcass (7–8 layers)	70	50	30	—
Carcass (5–6 layers)	70	50	30	—
Carcass (1–4 layers)	180	50	30–50	20–30

The plasticity of the stocks, which at 60 to 70° lies in the range 0.15 to 0.40, ensures a reliable bond between extruded components.

2) Experiments on the determination of scorching during rapid heating (raising the temperature in a period of 1 min and holding at the temperature reached for 20 min) show that in these conditions stocks going into tire casings may be heated as follows: tread stock up to 80°, breaker stock up to 60 to 70°, carcass stock (5 to 8 layers) up to 60 to 70°, carcass stock (1 to 4 layers) up to 80 to 100° without risk of scorching.

TABLE II

TEMPERATURE OF PORE FORMATION AND SPECIFIC VOLUMETRIC EXPANSION OF TIRE STOCKS DURING HEATING

Characteristic	Stock: Tread	Breaker	Carcass (7–8 layers)	Carcass (5–6 layers)	Carcass (1–4 layers)
Specific volumetric expansion $^\circ C^{-1} \cdot 10^4$	8–10	8–9	7–9	6–7	5–7
Threshold temperature for pore formation, ° C	94	73	80	90	109

3) The permissible time of holding tire stocks heated to various temperatures is shown in Table I.

4) The specific volumetric expansion of the stocks and the threshold temperature for intensive pore formation are given in Table II.

It should be noted that in the conditions of free heating of a raw tire cover the pore formation commences at the same temperatures at which pore formation takes place in testing on the special apparatus (of A. P. Pukhov). In a number of cases the pore formation sets a limit to the temperature of preliminary heating, as pore formation may take place at a temperature lower than the temperature of scorching. Pore formation is linked with the evaporation of the moisture from the stocks.

From the data obtained, taken as a whole, we came to the conclusion that it is necessary to heat the blanks up to 60 to 70° in the breaker and the upper layers of the carcass, and that it is desirable to hold them for a short period (of the order of 20 to 30 min) at the temperatures attained, prior to placing in the vulcanization apparatus.

In order to select the heating method we compared: heating of the raw casings by heat transfer from hot air (an external source of heat) and electric heating by high frequency currents (an internal source of heat). In Tables III and IV we give data characterizing the temperature distribution during heating of molded and unmolded casings by these methods.

TABLE III

HEATING OF MOLDED AND UNMOLDED TIRE CASING COMPONENTS BY HOT AIR

Casing size	Air temperature, ° C	Rate of circulation of air, m/sec	Temperature of component, ° C: Breaker: Crown	Breaker: Shoulder	Tread: On running surface	Tread: Center of the rubber mass	Carcass: 6th layer	Carcass: 1st layer	Bead	Time of heating, min
Unmolded components										
260–20	60	0	57	57	69	—	57	60	—	205
260–20	80	0	60	70	72	65	60	—	—	105
210–20	80	0	60	—	73	—	60	69	—	110
210–20	80	1	61	—	68	—	64	70	—	70
210–20	90	0	60	—	69	—	60	67	—	85–95
210–20	90	1	60	—	78	—	63	75	—	45
210–20	100	0	60	—	68	—	61	75	—	80
210–20	100	1	60	—	75	—	—	80	—	35
Molded components										
260–20	80–85	0	60	65–67	73	68–70	56–50	52–56	66–70	100–130
260–20	100–105	0	60	71	81	73	55	49	71	75–80
260–20	100–105	1	60	75	86	69	45	39	70	35–40

On consideration of these tables, we reach conclusions 1 and 2:

1. Hot air heating of the raw casings by any of the cycles leads to scorching of the separate components of the covers. The temperature distribution is unfavorable, since the surface of the tread and the 1st layer of the carcass get heated the most.

2. H.f. electric heating, even when carried out comparatively slowly (as a result of inadequate capacity in the apparatus employed) allows of heating up to 60° in the breaker and the carcass without scorching of the components and gives a favorable distribution of temperature in the casing (greatest heating of the breaker, carcass and air bag). The temperature distribution in h.f. electric heating, in contrast with heat-transfer heating, may be controlled by the shape of the electrodes.

As a result of the tests it was decided to settle for the electric heating method, after checking on the influence of the preliminary heating upon the quality of the casings. In Tables V and VI we give the results of the test stand resiliometer testing of casings produced with various cycles of thermal treatment.

From Tables V and VI the following conclusions 1) to 4) may be drawn:

1) Preliminary heating increases the serviceability in laboratory tests. The best variation is two-fold heating before molding and before vulcanization.

TABLE IV

ELECTRIC HEATING OF MOLDED AND UNMOLDED TIRE CASING COMPONENTS BY H.F. CURRENT

Casing size	Temperature of component, ° C											Temperature in air bag, ° C	Time of heating, min
	Sidewall		Shoulder			Crown							
	Surface	1st layer of carcass	Tread surface	1st layer of carcass	Breaker	Tread surface	Center of rubber mass	Breaker	6th layer of carcass	1st layer of carcass	Bead		
Unmolded tire covers													
210–20	50	60	45	60	55	45	50	55	60	56	50	—	11
260–20	—	—	—	65	63	47	—	63	62	60	56	—	10
Molded tire covers													
260–20	40.5	52*	—	58*	54	42	47	62	80*	86	50	96	12–15
260–20	—	70	—	—	—	48	—	62	—	90	53	100	12–15

* Measured in 4th layer of carcass.

TABLE V

TEST STAND RESILIOMETER. TESTS OF 260–20 TIRE CASINGS

	Tire casing characteristics	Test stand kilometers: Average	Maximum	Minimum	$\frac{K \text{ max.}}{K \text{ min.}}$	Km, % of km of reference sample
1	Production models from Yaroslavl Tire Works (100% synthetic rubber)	1996	5423	573	9.5	79
2	Experimental, with increased content of natural rubber	5778	10816	1503	7.2	225
3	Experimental, 100% synthetic rubber (reference sample)	2519	7429	310	24	100
4	Experimental, 100% synthetic rubber, h.f. heated before molding	4160	8450	790	10.7	165
5	Experimental, 100% synthetic rubber, h.f. heated after building.	4863	11570	1336	8.6	193
6	Experimental, 100% synthetic rubber, h.f. heated before vulcanization	6056	15080	560	26	240
7	Experimental, 100% synthetic rubber, h.f. heated before molding and before vulcanization	8930	11543	4720	2.4	354
8	Experimental, 100% synthetic rubber, h.f. heated before, and after molding	8064	11053	4287	2.5	320

2) Preliminary heating of blanks (Table V, No. 5 and 8) is advisable also where the casings cool down before molding or placing in the vulcanization apparatus.

3) Heating markedly reduces the scatter of the mileage readings in laboratory tests.

4) Heat-treated covers of 100% synthetic rubber have a higher mileage (Table V, No. 6, 7 and 8) than those with natural rubber in the breaker and upper layers of the carcass.

Thus, preliminary heating of tire casings before molding and vulcanization, judging by the results of resiliometer tests, considerably improves their quality.

In order to check on the above data in actual service conditions 400 casings were prepared by the best form of heating (Table V, No. 7) and subjected to testing.

TABLE VI

TEST STAND TESTS OF 210–20 CASINGS

Casing characteristics	Average kilometerage on test stand, km
Casing prepared by ordinary technique (not heated)	1054
Casing heated before molding	5470
Casing heated before molding and before vulcanization	10650

We can judge the economic aspect of the question approximately on the basis of the following considerations.

In heating each casing we consume 3 kilowatt/hours of electric power, the cost of which is 40 kopecks. Along with the servicing of the equipment and its depreciation the cost of the thermal treatment is approximately 1 ruble per casing. The improvement in the mileage of a 260–20 casing by as little as 10% gives a saving of the order of 50 rubles. The cost of an electric heating chamber for an output of 1000 casings per 24 hours comes, according to a rough calculation, to some tens of thousands of rubles.

The above method of heat treatment of casings by high frequency currents is simple in execution and does not involve changes in compounding nor equipment.

COMPATIBILITY AS THE BASIC FACTOR IN THE ADHESION OF HIGH MOLECULAR WEIGHT MATERIALS *

V. I. Alekseenko, L. A. Bogoslavskaya, and I. U. Mishustin

The phenomenon of adhesion occurs in a variety of processes as in bonding to surfaces, in finishing (lacquers) and in covering of various surfaces with protective coatings that consist of high molecular weight materials, etc. A study of the phenomenon of adhesion has, therefore, great practical and theoretical importance. Although there are many papers devoted to the investigation of the phenomenon there is yet no firmly established point of view as to its exact nature.

Autoadhesion and adhesion of high polymers is explained by Voyutskii[1] as depending on their ability to diffuse through each other and good compatibility of them is related to the ability of the macromolecules to mutually diffuse. In the case of incompatible polymers, adhesion is absent. Compatibility of high polymers as indicated by Alekseenko, Mishustin, and Voyutskii[2] is related to their polarity. High molecular weight polymers are only compatible if they are of equal or nearly equal polarity. Meisner and Merril[3] indicated that coalescence occurs at their respective transition temperatures. These temperatures are considerably lowered through addition of plasticizers to the high polymers. Tinius[4] indicates that for strong adhesion of two film-forming materials they must be of closely related polarity. A series of examples confirms these conceptions. Thus, polar nitrocellulose adheres poorly to nonpolar polyisobutylene and polystyrene.

The compatibility of polymers depends also on their molecular structure. Without a doubt the structure of high polymers has bearing on their adhesive properties. For example, natural rubber has a chemical composition similar to gutta percha, but differs from it in spatial configuration: natural rubber is the *cis* isomer and gutta percha the *trans*. The adhesive abilities of these compounds are also different: in the nonvulcanized state, natural rubber has low strength while gutta percha is fairly strong.

Nairit and Nairit-NT differ in a related manner. Nairit is a mixture containing a small number of *cis* monomer units and large amount (80%) of *trans* units, while Nairit-NT contains 90% of *trans* chloroprene units. The *cis* containing material has poor physicomechanical properties in the nonvulcanized state while the *trans* material has remarkably good properties.

In this paper we hope to fill a gap in the investigation of adhesion phenomena —that of establishing a relation between adhesion and compatibility of polymers. By using a variety of high molecular weight compounds in our investigation, we hoped to add to the present state of general knowledge of the adhesion phenomena and also to broaden the concept of compatibility of high polymers.

* Translated for Rubber Chemistry and Technology from *Kauchuk i Rezina* 16, No. 8, pages 10–15 (1957).

EXPERIMENTAL PART

As initial adhesives we used natural rubber (smoked sheet), gutta percha, Nairit/Nairit-NT, nitrocellulose dissolved in organic solvents (adhesive AGO) containing 15% dibutyl phthalate with respect to dry material, and polychloroethylene (vinyl chloride).

Nairit-NT has a higher specific gravity than common Nairit. This is explained by tighter packing of this polymer for which the degree of crystallization[6] is equal to 38% while the value for the common polymer is 12%. According to infrared data, Nairit-NT contains 90% of *trans* 1,4 units, 8% *cis* 1,4 units, 1% 1,2, and 1% of 3,4-chloroprene units.

Solutions of the adhesives mentioned were used to carry out experiments of bonding coated fabric (kirza) to rubber, leather to rubber, and rubber to rubber.

Compounds were made from butadiene-acrylonitrile copolymer (SKN-40) and butadiene-styrene copolymer (SKS-30) according to the following formulations.

	Compound	
	No. 1	No. 2
SKN-40	100	—
SKS-30	—	100
Ruberax	—	5
ZnO	5	5
Stearic acid	1.5	2
MBTS	—	0.6
Diphenylguanidine	—	0.75
MBT	0.8	—
Sulfur	1.5	2.4

In order to facilitate recognition of the effect of the type of rubber on bond strength, fillers were not used in the compounding.

Vulcanization was carried out at 145° C for 40 minutes. The vulcanizates had the following physical properties:

	No. 1	No. 2
Tensile, kg/cm²	42.0	26
Relative elongation, %	661	368
Permanent set, %	11.5	2.0

Usually rubber soles are treated with sulfuric acid before bonding to the upper part of the shoe (leather or textile). The role of this treatment of soles according to Voyutskiĭ, Rebinder, Khoroshevi, and Shur consists of increasing the polarity of the surface of the rubber. In this process the addition of polar sulfuric acid groups to the surface molecules of the rubber takes place. The increase in polarity of the surface leads to an increase of intermolecular forces between rubber and the polar material of the adhesive film, and also to an improved solubility of the polar adhesive in the rubber. All this results in better bonding.

Experiments in bonding soles with an adhesive made of Nairit-A showed that in this case the sulfuric acid treatment was not required which finding considerably simplified the building up process.

We did bonding experiments with compounds of Formulas 1 and 2 to fabric, to leather, and to rubber. The rubber stock was treated with sulfuric acid in some cases and in others untreated stock was used. These experiments simulated the process of bonding rubber soles to the uppers of shoes made of fabric, leather, and other materials.

A method of bonding was worked out in the Central Research Insitute of the Leather and Shoe Industry for various adhesives. For each adhesive, an optimum formula was used. In the case of a *cement made from natural rubber (No. 44-b)* both surfaces were coated twice with the cement and drying continued for 40 minutes. The surfaces were pressed together for 15 minutes. Neither heating nor refreshing of the cement was done before pressing. For *the cement made from gutta percha (No. 23/15)* the test strips made of leather or fabric were coated twice with cement. They were dried for 15 and 30 minutes. The rubber strips were coated once and dried for 30 minutes. Before bonding the strips were heated in a 100° thermostated oven for 10 minutes and, subsequently, pressed together for 15 minutes. For *the cement made from Nairit*

TABLE I

RESULTS OF ADHESION TESTS OF RUBBERS WITH MATERIALS USED FOR MAKING THE UPPER PART OF SHOES

Surfaces to be bonded	Rubber treated with H_2SO_4		Untreated rubber	
	Peel strength, kg	Peeling character	Peel strength, kg	Peeling character
Cement made from natural rubber (No. 44-B)				
SKN-40 to fabric	0.39	Adhesive film from rubber	1.31	Adhesive film from rubber
SKS-30 to fabric	0.60	The same	2.12	The same
SKN-40 to leather	0.53	The same	1.33	The same
SKS-30 to leather	0.62	The same	2.13	The same
SKN-40 to rubber SKN-40	0.88	The same	1.40	The same
SKS-30 to rubber SKS-30	0.85	The same	2.00	The same
SKN-40 to SKS-30	0.63	The same	1.36	The same
Cement made from gutta percha (No. 23/15)				
SKN-40 to fabric	1.85	Adhesive film from rubber	2.05	Adhesive film from rubber
SKS-30 to fabric	1.53	The same	6.70	The same
SKN-40 to leather	1.20	The same	1.70	The same
SKS-30 to leather	1.45	The same	5.00	Along adhesive film and rubber
SKN-40 to SKN-40	1.23	The same	1.83	A.F.f.R.[a]
SKS-30 to SKS-30	1.65	The same	4.65	A.A.F.a.R.[b]
SKN-40 to SKS-30	1.20	The same	1.50	A.F.f.R.
Cement made from Nairit (No. 10)				
SKN-40 to fabric	2.00	Adhesive film from rubber	5.03	Along adhesive film
SKS-30 to fabric	2.10	The same	2.44	A.F.f.R.
SKN-40 to leather	2.20	The same	5.05	A.A.F.a.R.
SKS-30 to leather	2.14	The same	2.55	A.F.f.R.
SKN-40 to SKN-40	2.20	The same	4.80	A.A.F.a.R.
SKS-30 to SKS-30	2.43	The same	2.55	A.A.F.a.R.
SKN-40 to SKS-30	2.24	The same	2.85	A.F.f.R.
Cement made from Nairit-NT (No. 241)				
SKN-40 to fabric	3.40	A.F.f.R.[a]	8.35	Along rubber
SKS-30 to fabric	5.00	Along rubber	4.80	Along rubber
SKN-40 to leather	2.73	A.F.f.R.	8.25	Along rubber
SKS-30 to leather	5.80	Along rubber	4.60	Along rubber
SKN-40 to SKN-40	3.95	A.F.f.R.	5.65	Along rubber
SKS-30 to SKS-30	5.70	Along rubber	3.35	Along rubber
SKN-40 to SKS-30	5.00	Along rubber	4.55	Along rubber

TABLE I—*Continued*

Surfaces to be bonded	Rubber treated with H_2SO_4: Peel strength, kg	Rubber treated with H_2SO_4: Peeling character	Untreated rubber: Peel strength, kg	Untreated rubber: Peeling character
Cement made from nitrocellulose (AGO)				
SKN-40 to fabric	14.45	Along rubber	12.25	Along rubber
SKS-30 to fabric	1.40	A.F.f.R.	0.18	A.F.f.R.
SKN-40 to leather	13.30	Along rubber	11.1	Along rubber
SKS-30 to leather	5.00	Along rubber	0.18	A.F.f. rubber
SKS-30 to SKS-30	10.45	Along rubber	10.16	Along rubber
SKN-40 to SKS-30	0.57	A.F.f.R. and along rubber	0.23 0.19	Along rubber
Cement made from polychloroethylene				
SKN-40 to fabric	4.30	A.F.f.R. and along rubber	10.00	Along rubber
SKS-30 to fabric	1.05	A.F.f.R. and along rubber	0.35	A.F.f.R.
SKN-40 to leather	6.05	Along rubber	9.95	Along rubber
SKS-30 to leather	1.00	A.F.f.R.	0.25	A.F.f.R.
SKS-40 to SKS-40	3.60	A.F.f.R. and along rubber	7.05	A.F.f.R.
SKS-30 to SKS-30	1.40	A.F.f.R.	0.20	A.A.f.a.R.
SKN-40 to SKS-30	1.25	A.F.f.R.	0.20	A.F.f.R.

[a] A.F.f.R.—Adhesive film from rubber.
[b] A.A.F.a.R.—Along adhesive film and rubber.

(*No. 10*) both surfaces were coated once with the cement. They were dried for 40 minutes and pressed together for 15 minutes. Before bonding the samples were neither heated nor refreshed. For *the cement made from Nairit-NT* (*No. 241*) both surfaces were coated once; they were dried for 40 minutes. Before bonding the rubber strip was heated under a reflector for 1.5 minutes at 150°. The strips were pressed together for 15 minutes. For *the cement made from polychloroethylene* (*No. 37*) *and from nitrocellulose* (*AGO*) both surfaces were coated twice with cement and subsequently dried for 45 minutes. The coated strips were stored for 24 hours and refreshed with solvent before bonding. The

TABLE II

PHYSICAL PROPERTIES OF FILMS MADE OF 1:1 ADHESIVE–RUBBER COMPOUND MIXTURES

The compound being the same as that from which the vulcanizates were made

Composition of mixture	Physical properties of the films: Tensile strength, kg/cm²	Physical properties of the films: Elongation, %
Natural rubber and SKN-40	1.0	1400
Natural rubber and SKS-30	2.0	1000
Gutta percha and SKN-40	40	170
Gutta percha and SKS-30	60	200
Nairit and SKN-40	33	1350
Nairit and SKS-30	24	1200
Nairit-NT and SKN-40	82	1100
Nairit-NT and SKS-30	60	1000
Nitrocellulose and SKN-40	150	166
Nitrocellulose and SKS-30	80	229
Polychloroethylene and SKN-40	139	420
Polychloroethylene and SKS-30	9	22

strips were pressed together for 15 minutes and stored for 24 hours before the bond strength was tested by peeling.

In this investigation, the character of the peeling was noted. The results are given in Table I for rubber treated with sulfuric acid and for untreated rubber.

To establish the relationship between strength of adhesion and compatibility of the adhesive with the materials to be cemented together, physical chemical properties of films made from the adhesives and rubbers were determined, vulcanizates being made from a 1:1 ratio.

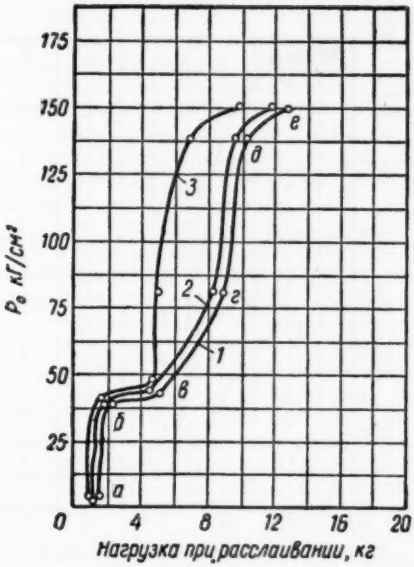

FIG. 1.—Relation between tensile strength (the ordinate, in kg) of compatible polymers and peel strength (the abscissa, in kg) of the joints made with sulfuric acid treated rubber. Curve *1*: joints made from SKN-40 rubber to fabric. Curve *2*: SKN-40 to leather. Curve *3*: SKN-40 to SKN-40. The data depend on the cement: lowest group of data (a) cement made of natural rubber; next highest group (b) gutta percha with Nairit cement; next highest group (g) Nairit-NT cement; next highest group (d) polychloroethylene cement; and the highest group of data are for joints made from nitrocellulose cement (e).

The films made from natural rubber, gutta percha, Nairit, and polychloroethylene were prepared by mixing these substances with rubbers (SKN-40 and SKS-30) on the mill and subsequent pressing at 150° for 10 minutes. The films from nitrocellulose and rubber were prepared by drying the solutions at room temperature and subsequent heating to 70° for 2 hours. The results of the film tests are given in Table II. Figure 1 and 2 curves are presented to show the relationship between bond strength (peel test) obtained using untreated rubber made from SKN-40 and values for tensile strength and elongation of the films made from the mixtures of adhesive and rubber from which the vulcanizates were made.

From Table I, it becomes apparent that cement made from natural rubber gave the poorest bond strength compared to the other adhesives that were investigated when used in bonding of fabrics, leather, and rubber with rubber (SKN-40 and SKS-30). The cement made from gutta percha gave better

bond strength than natural rubber cement. With both cements it was found that the strength of the adhesive bond was higher with untreated SKS-30 than with untreated SKN-40 rubber. For both cements it was also found that the peel strength was higher in the case of untreated rubber than with sulfuric acid-treated surfaces. The cement made from Nairit gives bonds of lower strength than that made from Nairit-NT. Cements made from Nairit and Nairit-NT give stronger bonds with SKN-40 than with SKS-30. Practically the same results were obtained with treated and untreated SKS-30 rubber. Nairit-NT gives higher peel strength with SKS-30.

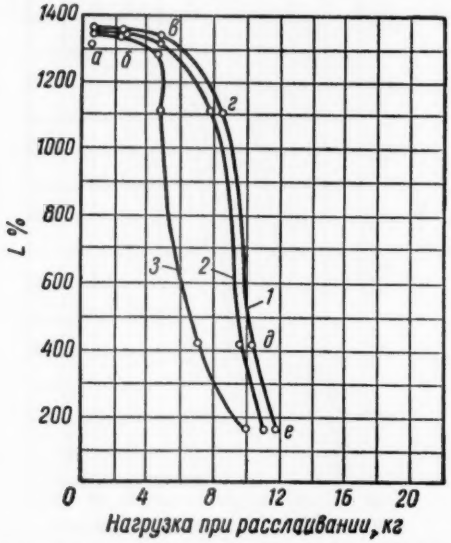

FIG. 2.—Relation between elongation (ordinate, %) of compatible polymers and bond strength (abscissa, kg, peel force) for joints made of untreated rubber. Curve *1*: joints made from SKN-40 to fabric. Curve *2*: SKN-40 to leather. Curve *3*: SKN-40 to SKN-40. The data depend on the cement; reading from upper left to lower right the cements were: (a) cement made from natural rubber, (b) guttapercha with Nairit, (g) Nairit-NT, (d) polychloroethylene, and (e) nitrocellulose.

Cements made from nitrocellulose gave the highest bond strength of all adhesives used when used for adhering fabrics, leather, and rubber to SKN-40. Lower peel strength was obtained when bonding to SKS-30 rubber, when bonding fabrics and especially leather to treated SKS-30; higher bond strengths were obtained than with untreated rubber. Polychloroethylene cement gives higher strength bonds with SKN-40 rubber than with SKS-30. Treated SKN-40 gave lower strength bonds than untreated SKN-40; however, the reverse relationship was found to hold for SKS-30.

DISCUSSION

Alekseenko, Mishustin, and Voyutskiĭ have found that the compatibility of nitrocellulose with SKN-26 type rubber is borne out by high tensile strength of films made from blends of these materials. Also, the compatibility of polychloroethylene with SKN-26 is borne out by high tensile strength that we observed in films made from mixtures of these substances. Films made from

mixtures of nitrocellulose with SKS-30 rubber and also polychloroethylene with SKS-30 showed very low tensile strength. This indicates that these materials are incompatible with one another. These data coincide with those obtained from measuring bond strength on joints cemented with nitrocellulose and polychloroethylene. High bond strength was observed for joints made with nitrocellulose-polychloroethylene cements and SKN-40 rubbers; low strength bonds were obtained with the same cements on SKS-30 rubber. This is a good indication that on bonding materials with cements made of compatible substances, diffusion of the macromolecules of the cement occur into the surface of the materials to be bonded. As a result, the adhesion between the materials that are bonded increases. Voyutskii[1] was the first to emphasize the importance of compatibility in the adhesion of high polymers. Deryagin, Zherebov, and Medvedeva[7] also noted the importance of diffusion of polymer chains and compatibility on adhesion of rubbers. Earlier, Alekseenko, Mishustin, and Voyutskii[2], and also Alekseenko and Mishustin[8,9], showed that the compatibility of butadiene-acrylonitrile rubber with nitrocellulose, butadiene-vinylidene chloride rubber with polyvinyl chloride and with polyvinyl acetate, various types of synthetic and natural rubbers correlate with the polarity of these polymers. Best compatibilities are shown by the polymers with similar values of dielectric permeability which is an indication of their polarity. The phenomenon of adhesion is determined by the diffusion of macromolecular chains and their fragments into the adhering surfaces. As a rule, higher strength bonds were obtained with polar adhesives. The structure of the adhesive plays an important role in adhesion. The cement made from natural rubber which is the *cis* isomer of polyisoprene, gives lower strength bonds than the one made of gutta percha which is *trans*. The same was found to be true for adhesives made from Nairit and Nairit-NT. Cements made from nonpolar polymers gave higher bond strength with joints made from nonpolar SKS-30; cements made from polar polymers gave higher peel strength with joints made from polar SKN-40 or with sulfuric acid-treated SKS-30 surfaces. This treatment increases the polarity of the surface.

From Figures 1 and 2, it becomes apparent that the bond strengths vary directly with the tensile strength and indirectly with the elongation of compatible polymers. The bond strength variation as a function of the tensile strength in the case of joints made from rubber and fabric is almost the same as in the case of leather-rubber joints (Curves *1* and *2* in Figures 1 and 2 almost coincide); the plots of bond strengths of rubber to rubber joints follow the same general law as for the two previous cases, but their absolute values are generally lower. This can be explained by the fact that the polar properties of the adhesives and SKN-40 or SKS-30 rubber differ more from each other than the polar properties of adhesives and the materials of the uppers of shoes (fabric and leather). The fabric consists of cellulose and leather of albuminous substances of which gelatin can serve as a model. Values of dielectric permeability[10–13], which characterize the polar properties of the materials investigated by us, are as follows:

Natural rubber	2.45
SKS-30	2.75
SKN-40	16.00
Gutta percha	2.6
Nairit and Nairit-NT	3.0
Polychloroethylene	4.0
Nitrocellulose	8.0
Cellulose	6.7
Gelatin	7.6

From these data, it is apparent that the dielectric permeability of nitrocellulose, gelatin, and cellulose are very similar. This should explain the high strength bonds obtained with nitrocellulose cement in rubber to leather and fabric joints.

Voyutskiĭ and Shtarkh[14] established that the bond strength of SKN-40 rubber joints at elevated temperature is high. These same joints exhibit low peel strength at ambient temperatures. This phenomenon may be explained by the fact that thermal motion, and thereby, diffusion is increased at elevated temperature. Therefore, adhesive films are heated with reflectors in industrial production before pressing the soles and the upper part of the shoe together.

Moses[15] in his paper reported that good adhesion can be obtained between surfaces if the adhesive film on heating is softened or liquefied. Tinius[4] found that adhesion between surfaces is greater, the higher the bonding energy of the atom groups of the macromolecules of the adhesive. In order to get good adhesion, this energy should not be less than 5000 cal/mole characteristic for polar macromolecular compounds. Our results show that this requirement is not always essential. The spatial configuration of the high polymer has a great influence on adhesion strength. The reason for this fact has not yet been clarified.

SUMMARY

1. Relationships were established between the bond strength of joints made from rubber with fabric, leather, or rubber with physical property data from the films made from the mixtures of the adhesive with the rubber from which the vulcanizates were made.

2. The effect of the chemical structure of the adhesive on the bond strength is established.

3. Nairit-NT, mainly the *trans* isomer of poly-1,4-chloroprene and chemically closely related to gutta percha (*trans* polyisoprene) gives a good adhesive cement for bonding rubber to fabric, leather, or rubber. It makes chemical surface treatment unnecessary. This new adhesive gives good bonding to SKS-30. Similar results were obtained with cement made from gutta percha; however, bonding strength to SKN-40 rubber was much higher.

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EFFECT OF HIGH PRESSURE ON SELF ADHESION (AUTOHESION) OF HIGH POLYMERS *

L. A. Igonin, Yu. V. Ovchinnikov, and S. A. Arzhakov

The phenomenon of self adhesion of high polymers is one of the very important but little studied properties of these materials. Self adhesion of rubberlike polymers has been studied[1–4], but there is little work reported on the self adhesion of thermoplastics. There is, however, no doubt about the importance of the role of this phenomenon in the process of producing products from powdered and granular thermoplastics.

The influence of temperature and pressure on the self adhesion of some thermoplastic powders was studied in the present work. The conditions for the formation of a transparent sample were found by pressing the powdered material in a heated cylindrical press. The samples pressed were 10 mm in diameter and 4–5 mm thick. The temperature and pressure were varied over a wide range.

The samples were pressed in the following manner: The polymer sample was placed in the cold press and a given pressure was applied; the temperature was then raised to a given value and the sample was held at this temperature for 15 minutes; after cooling the press to 50–60° the pressure was released, the sample was removed from the press and the density to visible light was evaluated visually.

When a transparent sample is obtained by pressing the thermoplastic polymer, partial or complete coalescence of the grains of the material takes place with a disappearance of grain boundaries. Under these conditions the strength of the sample may not reach the cohesive strength of the material as has sometimes been assumed[5].

Figure 1 shows the change in thickness of transparent samples of polyvinyl chloride annealed at 100° for 15 minutes. The data were obtained by means of dynamometric weights which were used as a thickness gauge in this case. The samples were pressed at different temperatures with a pressure of 400 kg/cm^2 and a 15 minute pressing time. It follows from Figure 1 that samples pressed at temperatures up to 130° change considerably in size on annealing. They also lose their transparency and become more white. Samples which are pressed at higher temperatures are stable on annealing and retain their size and transparency.

Therefore, only partial coalescence of polymer grains takes place at temperatures below 130°, and only at higher temperatures does the strength of the samples reach the cohesive strength of the material. When pressing of the polymer powder produces non-transparent samples self adhesion does not occur.

Figure 2 is the P-T curve for polyvinyl chloride, showing the temperatures and pressures at which transparent samples are formed. From these data it follows that self adhesion of polyvinyl chloride begins at temperatures 5–10°

* Translated by Theodor Tarasjuk, Katherine and Willard P. Tyler for Rubber Chemistry and Technology, from *Doklady Akad. Nauk SSSR* 120, 1062–1064 (1958).

above the vitrification temperature (glass point). It is also seen that the border line dividing the regions of formation of transparent and of non-transparent samples lies in the region from 100–150 kg/cm².

Thus an increase in pressure at a given temperature produces non-transparent samples up to the pressure limit set by the lower branch of the curve. This region corresponds to the growth of the general contact area of the grains, an apparently necessary condition for the appearance of self adhesion. Further

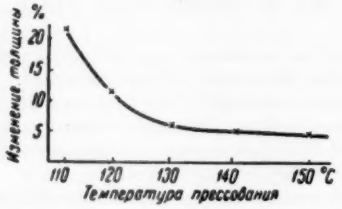

FIG. 1.—Change in thickness of transparent samples of polyvinyl chloride on annealing. Abscissa; temperature of press. Ordinate; change in thickness.

increase of pressure leads to the formation of transparent samples; that is, to disappearance of grain boundaries in the material because of complete or partial coalescence. As was pointed out before, complete coalescence of polyvinyl chloride in the given annealing time takes place at temperatures exceeding T_g by 50°; that is, above 130°.

The upper branch of the curve gives the limiting pressure above which again only non-transparent samples are obtained. At these pressures self adhesion

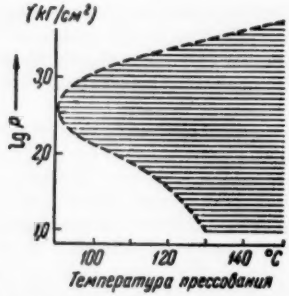

FIG. 2.—Region of formation of transparent polyvinyl chloride. Abscissa; temperature of press. Ordinate; log P, (kg/cm²).

of the material does not occur. The presence of the upper branch could be explained by the increase in stiffness of the polyvinyl chloride polymer chain which begins to be noticeable at pressures exceeding 1000 kg/cm². Thus the vitrification temperature of the polymer increases and approaches the temperature of the press. This limits the self adhesion and causes the formation of nontransparent samples.

This condition is illustrated by the data shown in Figure 3. In this experiment the plunger of the press was connected with the indicator showing the

change of volume of the polymer powder in the press, and a rate of temperature increase of 1° per minute was used. Before heating the press a pressure was applied to the material corresponding to a value on the upper branch of the curve and this pressure was held constant during the experiment. In this case

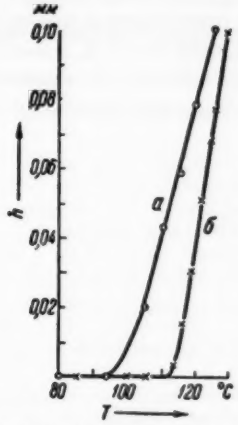

FIG. 3.—Change in volume of polyvinyl chloride powder in the press with increase in temperature. Abscissa; T. Ordinate; h, mm. a—Pressure, 1100 kg/cm²; b—Pressure, 2400 kg/cm².

it could be expected that the sharp change in volume would occur in the region of T_g because of the flow of the polymer to fill the free space in the press cavity. From Figure 3 it can be seen that for pressures of 1100 and 2400 kg/cm² the sharp change in volume occurred at 100 and 115°, respectively. This coincides closely with the points on the upper branch of the curve of Figure 2.

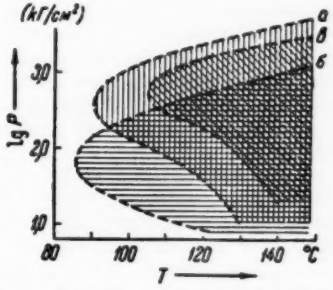

FIG. 4.—Regions of formation of transparent samples. Abscissa; T. Ordinate; log P (kg/cm²); a—Polyvinyl chloride (T_g=80°); b—Polystyrene block (T_g=80°); c—Polymethyl methacrylate ST-1 (T_g=115°).

The dependence of vitrification temperature of polyvinyl chloride on pressure was also observed on a number of other polymers. Figure 4 gives the P-T curves for polyvinyl chloride, polystyrene and polymethyl methacrylate.

Further illustration of this dependence was obtained by cutting two samples of the polymer from a sheet and pressing them together under the conditions

described above. In this case a single block of transparent sample was obtained only within the pressure range limited by the upper and lower branches of the curve.

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THE COAGULATION MECHANISM OF BUTADIENE–STYRENE LATEX *

S. A. Glikman and E. P. Korchagina

The Saratov State University, USSR

Most authors attribute the stability of synthetic latexes mainly to the presence on the globule surfaces of an electric double layer, formed as the result of ionization of adsorbed soap molecules[1]. It has been reported that the structural film formed by colloidal soaps has a protective action[2]. However, calculations based on data on globule size[3–5] show that the amounts of adsorbed substances are not enough to coat the globules even with a monomolecular layer. Data on the coagulation thresholds of latexes by various cations[1,6] are in general agreement with typical data for lyophobic sols. At the same time the role of univalent cations, the action of which can be compared with the staling-out effect[7,8], gives rise to doubt.

Extension of our knowledge of the nature of synthetic rubber latex coagulation by electrolytes, and of means of influencing the course of this process, is of theoretical and practical interest. In particular, in the production of butadiene–styrene rubber (SKS-30A) it would be desirable in many respects to replace calcium chloride, generally used for coagulation of the latex, by sodium chloride; but 40 times as much of the latter as of $CaCl_2$ is needed to coagulate the latex, and the resultant blanket is difficult to dry, owing to its structural peculiarities.

In order to investigate the nature of the action of mineral salts and certain other substances on the coagulation of SKS-30A latexes, we studied the effect of sodium and calcium chlorides and of certain nonelectrolytes on latexes at concentrations from 0.01 to 6%. The observations were carried out by means of a nephelometer 24 hours after preparation of the solutions. Aqueous solutions without added buffers were used, so that the influence of extraneous ions of buffer mixtures was excluded. The results are given in Figure 1. Figure 1 shows that the coagulation thresholds of the diluted latexes are 200 times as high for NaCl as for $CaCl_2$. The coagulation thresholds increase with increasing latex concentration, and the difference between the effects of Na^+ and Ca^{2+} diminishes somewhat. At the same time, the complete coagulation concentrations remain unchange at all latex concentrations, being 30 times greater for Na^+ than for Ca^{2+}. The absolute values of NaCl concentrations which cause complete coagulation even of concentrated latexes are several times less than the concentrations required for the salting-out effect. On the other hand, however, the fact that, for any latex concentration, equal amounts of Na^+ and Ca^{2+} are required for complete coagulation indicates that the role of electrolytes in latex coagulation is not confined to lowering the zeta potential. Our study[8] of the structural differences between the coagulation products obtained by the action of Na^+ and Ca^{2+}, and of the nature and porosity of the blankets formed

* Reprinted from the *Colloid Journal*, Vol. 19, pages 657–660 (1957); a translation by Consultants Bureau, Inc. of *Kolloidnyi Zhurnal* 19, 657–661 (1957).

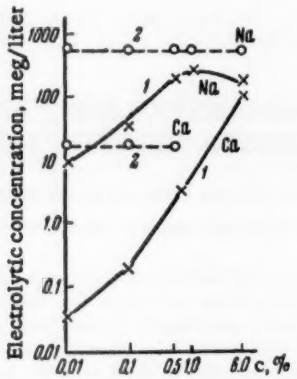

FIG. 1.—Variation of coagulation thresholds (*1*) and complete coagulation concentration (*2*) with concentration of SKS-30A latex (logarithmic scale).

from these products also indicates this. The nature of these differences is revealed by studies of the influence of certain nonelectrolytes on the course and character of the coagulation of SKS-30A latex.

Experiments showed that the coagulation threshold is not affected by addition of various amounts of hydroquinone to the latex. However, with an NaCl concentration which causes complete coagulation, the presence of 0.5% of hydroquinone in the latex gives a looser blanket, easier to dry. Addition of 2–5% hydroquinone to the latex makes blanket formation impossible, as with the amounts of NaCl used in the formulation a milky dispersion of very fine particles is formed, and visible coagulation does not occur at all. This dispersion, at a high degree of dilution with water, is as stable as the original latex; after it has been allowed to stand for many days not only does it show no signs of visible coagulation, but its turbidity remains quite unchanged.

Figure 2 shows the effect of concentration of rubber (in grams per 100 ml of liquid) on the relative light scattering (I/I_0, where I_0 is the light scattering of 0.01% latex) of dispersion with hydroquinone and of latex. These results show that at low concentrations of rubber in the latex light scattering is approxi-

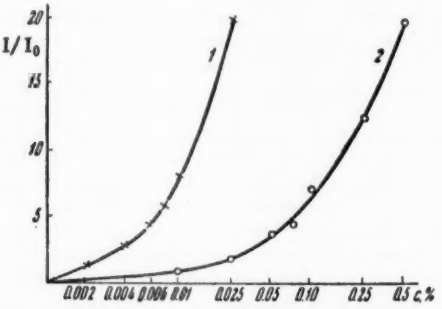

FIG. 2.—Effect of rubber concentration on the relative light scattering of dispersion containing hydroquinone (*1*) and of latex (*2*).

mately proportional to the concentration, in accordance with Rayleigh's law; at higher concentrations the relationship is no longer linear. On the average, for equal concentrations of rubber in the latex and the dispersion, $I_{disp}/I_{lat} \sim 10$. This means that the volume of a particle of the dispersion is about 10 times the volume of a globule of the uncoagulated latex.

A latex dispersion diluted to a low concentration immediately after coagulation by NaCl, without additional hydroquinone, does not differ in any respect from a diluted dispersion of the coagulated latex containing 5% hydroquinone. In 0.005% dispersions of both types negligible amounts of NaCl and hydroquinone are present; they consist of particles about 10 times the size of the original latex particles. Visible coagulation of these dispersions requires the addition of 2.5% NaCl. Complete coagulation (with formation of flakes and a transparent serum) is caused by addition of 3.0% NaCl. However, if before addition of NaCl 5% of hydroquinone is added to 0.005% dispersion (made from latex coagulated by the usual formula), then after 24 hours of standing only reversible "creaming" occurs, whereas in control experiments (without hydroquinone) irreversible flakes are formed. All these experiments indicate that the size of the primary particles in latex coagulated by sodium chloride does not depend on the presence of hydroquinone in the latex.

It has been shown[8] that the difference between the blankets formed from latex coagulated by Na^+ and Ca^{2+}, respectively, lies in their macrostructure, in the volume and form of the intermediate pores, and the associated macrocavities. The specific surface, which is largely determined by the presence of micropores, is almost the same for both types of blanket. If this is considered in conjunction with the fact, noted above, that the dimensions of the primary aggregates of rubber globules remain constant, the idea of two stages in the coagulation process naturally arises. The first stage is the result of a fall of the zeta potential to the critical value, and consists of primary aggregate formation; the second stage consists of coalescence of these aggregates. This is evidently the stage which determines the difference between the structures of the blankets.

In the case of coagulation by calcium chloride, the fixation of molecules of insoluble Ca soaps on the globule surfaces should play an important role. Here not only the steric factor, which results in the formation of a looser structure, but also the energy factor, which consolidates this structure owing to interaction between the Ca soap molecules, may be of significance. In latexes coagulated by sodium salts the primary globule aggregates may be protected from coalescence by molecules of other constituents of the latex, including hydroquinone molecules, adsorbed on these particles.

After decrease of the zeta potential the surface soap film is not sufficient to protect the latex particles from coalescence resulting from autohesion, as this film does not completely cover the globule surface. On the contrary, the presence of such an incomplete film may sometimes intensify cohesion and coalescence of the particles, if, for example, this film is formed by soaps with bivalent cations, as is the case at a concentration of $\sim 0.1\%$ $CaCl_2$. Here, regardless of the latex concentration, the $CaCl_2$ concentration plays the dominant role, since exchange adsorption is the factor which determines the state of the system. Coagulation of the latex by calcium chloride is not only an autohesion effect, but is also ionic in character, and this leads to formation of loose coagulation products. The structure of the latter is determined by a combination of the steric and energy factors (ionic bonds).

The effect of sodium chloride on the coalescence of the primary aggregated latex particles is in fact analogous to (but not identical with) salting-out. The effect occurs at relatively high NaCl concentrations (of the order of 3%), and does not depend on the concentration of the latex. The coalescence which takes place at a definite ratio of the interaction energies of the primary aggregates of latex globules with each other and with water, occurs at a certain limiting concentration of NaCl, in presence of which the adhesive power of water is diminished. Since the coalescence of the primary particles in the coagulation of latexes by NaCl is primarily due to autohesion, the secondary structures formed are dense, and this leads in its turn to the formation of a compact blanket, difficut to dry, typical of these conditions. The molecules of "diphilic" substances, which are adsorbed more vigorously by rubber but are less hydrophilic than soaps, may protect the uncharged and partially "stripped" (owing to desorption of soaps) particles of the coagulated latex from coalescence. Hydroquinone is evidently such a substance. If the amount of hydroquinone is insufficient, coalescence is not excluded but merely hindered, and other steric conditions are set up, so that the coagulum is looser.

Certain other nonelectrolytes exert an influence analogous to that of hydroquinone on the second stage of coagulation. Especially interesting results were obtained with phenol. The action of the latter was even more dependent on the concentration than the action of hydroquinone, and it also greatly depended on the concentrations of the latex and NaCl. In particular, it was found that in presence of 0.8% of phenol (on the weight of the latex) complete coagulation of the latex can be effected by addition of one-third of the amount of NaCl prescribed in the formulation, and the blanket formed from the coagulum is fully satisfactory and is dried more easily than the usual blanket obtained by NaCl coagulation of the latex.

The complex nature of the effects produced by the addition of different amounts of phenol to the latex can be explained by its twofold role. It seems that phenol, on the one hand, assists coagulation of the latex, and on the other, hinders coalescence of the coagulated particles. It seems possible that phenol molecules are not only adsorbed on the soap-free regions of the surface of the globules and their primary aggregates (or are solubilized in the soap film), but also partially displace the soap molecules from this surface. This is confirmed by variations of the soap concentration in the dispersion medium of the coagulated latex. It was shown by a conductometric titration method developed by Maron et al.[9] that serums of latexes to which 0.8% phenol had been added before coagulation by NaCl contained much higher concentrations of soap than control serums, formed under the usual coagulation conditions.

SUMMARY

1. It is shown that the absolute values of the coagulation thresholds of SKS-30A latexes diluted down to 0.01% correspond to the usual values for lyophobic sols. The values for NaCl are 200 times those for $CaCl_2$, and increase with the latex concentration. The complete coagulation concentration for NaCl is 30 times that for $CaCl_2$, and does not depend on the dilution of the latex.

2. It was shown by a nephelometric method that the volume of the primary particles formed in coagulation of the latex by sodium chloride is about 10 times the volume of the uncoagulated latex globules, irrespective of the latex concentration.

3. Consideration of the experimental data, in conjunction with facts reported in the literature, leads to the concept of two stages in the coagulation of latex by electrolytes: the first is the consequence of a decrease of the zeta potential, leading to the formation of primary particles, and the second leads to coalescence of these particles. The secondary aggregation processes can be prevented or modified by introduction of certain additives (nonelectrolytes) into the latex.

4. In additon to an explanation of the mechanism of latex coagulation by electrolytes, and a demonstration that this process can be controlled, indications are given of means of an approach to development of conditions for the production of a good blanket by coagulation of latex by sodium chloride, with a much decreased consumption of the latter.

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THE STRUCTURE OF GELS. IX. EFFECTS OF PLASTICIZERS ON THE PHYSICAL PROPERTIES OF STYRENE BUTADIENE RUBBER

M. P. Zverev and P. I. Zubov

The L. ya. Karpov Physicochemical Institute, USSR

It was shown in the previous communication[1] that plasticizing of high polymers, like the swelling process, involves not only weakening of the forces between the macromolecules, but also changes in their form. The greatest plasticizing effect in styrene butadiene rubber was produced by nonpolar plasticizers. The present paper contains experimental data on the influence of the plasticizer structure (polarity) on the physical properties of SKS-30 A styrene butadiene rubber and its vulcanizate. The composition of the mix, vulcanization conditions, and plasticizers were the same as before[1]. The effect of the nature of the plasticizer on the temperatures of transition of the polymer from one physical state into another was studied with the aid of Kargin's dynamometric balance[2]. The mechanical strength of unfilled vulcanizates, calculated on the initial cross section, was determined by means of a dynamometer of the Polanyi type. The maximum error was $\pm 5\%$. The vulcanization optimum was established from the equilibrium modulus[3].

Kargin and Malinski [4] showed that the magnitude of the plasticizing effect for nonpolar polymers is a linear function of the volume fraction of the plasticizer in the polymer. It was of interest to determine to what extent the volume fraction rule applies to styrene butadiene rubber.

Table I shows the variations of the glass transition temperature of rubber with the volume fraction of the plasticizer.

Table I shows that at low plasticizer concentrations in the rubber the volume fraction rule is obeyed fairly satisfactorily; the decrease of the glass transition temperature does not depend on the nature of the plasticizer. Deviations from this rule are found at higher concentrations. In such conditions the glass transition temperature is lower in presence of nonpolar than of polar plasticizers.

Table I also gives data on the influence of the nature of the plasticizer on the temperature of transition of styrene butadiene rubber into the viscofluid state; these results show that considerable increases of the flow temperature of rubber are also produced by nonpolar plasticizers. We also investigated the effects of plasticizer structure on the mechanical strength and relative extension of the unfilled vulcanizate. The results are given in Table II.

Table II shows that in presence of small amounts of plasticizer in the vulcanizate the decrease of tensile strength and the change of relative extension are practically independent of the plasticizer structure. The effects of molecular structure of the plasticizer become noticeable above 20%. With 50%

* Reprinted from the *Colloid Journal*, Vol. 19, pages 211–213 (1957); a translation of *Kolloidnyi Zhurnal* 19, 201–203 (1957) by the Consultants Bureau, Inc.

TABLE I

VARIATIONS OF THE GLASS AND FLOW TEMPERATURES OF RUBBER WITH THE VOLUME FRACTION OF THE PLASTICIZER

Plasticizer	Amount of plasticizer in volume %							
	5	10	20	30	50	5	10	20
	Glass transition temperature of rubber in ° C					Flow temperature of rubber in ° C		
Tetralin	−53	−56	−63	−70	−77	146	127	99
Green oil	−53	−57	−65	-72	−78	140	122	92
Ditolylmethane	−55	−58	−66	−76	−85	135	117	84
Dicumylmethane	−54	−58	−68	−77	−85	137	118	85
Dibutyl sebacate	−58	−63	−70	−81	−89	133	110	80
Dibutyl phthalate	−55	−60	−69	−82	−90	134	108	78
Diethyl phthalate*	−55	−60	−68	—	—	130	108	80
	−55	−58	−70	—	—	130	108	78

* Only up to 20% of diethyl phthalate and tricresyl phthalate was added to the rubber, as larger amounts of these plasticizers were not compatible with the polymer.

plasticizer the mechanical strength and the relative extension of specimens plasticized with tetralin or green oil are approximately 25–30%, and the relative extension is 50–60%, higher than the strength and the relative extension of specimens plasticized with phthalate or sebacate esters.

SUMMARY

1. The glass and flow temperatures and the strength and relative extension of rubber depend not only on the concentration of the plasticizer but also on its molecular structure.

2. Styrene butadiene rubber plasticized with nonpolar plasticizers has higher glass and flow transition temperatures than rubber plasticized with

TABLE II

EFFECT OF PLASTICIZER STRUCTURE ON THE TENSILE STRENGTH AND RELATIVE EXTENSION OF UNFILLED VULCANIZATE

Plasticizer	Amount of plasticizer in volume %				
	5	10	20	30	50
	Tensile strength in kg/cm²				
Tetralin	16.1	14.3	12.0	9.8	7.8
Green oil	15.8	14.6	11.6	9.2	7.3
Ditolylmethane	15.7	13.9	10.7	8.8	6.5
Dicumylmethane	16.0	14.3	11.4	9.0	6.4
Dibutyl sebacate	15.7	13.6	10.6	8.6	5.8
Dibutyl phthalate	15.6	13.8	10.9	8.4	5.8
Diethyl phthalate	16.1	14.0	10.6	—	—
Tricresyl phosphate	15.8	14.3	10.5	—	—
	Relative extension in %				
Tetraline	570	580	540	530	490
Green oil	600	570	550	520	480
Ditolylmethane	590	570	540	520	450
Dicumylmethane	570	560	540	510	450
Dibutyl sebacate	570	560	550	500	420
Diethyl phthalate	570	580	540	—	—
Tricresyl phosphate	570	570	540	—	—

polar substances. The same relationships are found for the strength and relative extension of vulcanizates of this rubber.

3. Nonpolar plasticizers also weaken intramolecular interaction to a greater extent than polar plasticizers.

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THE STRUCTURE OF GELS. X. GLOBULIZATION OF RUBBER UNDER THE ACTION OF NONSOLVENTS *

P. I. Zubov, Z. N. Zhurkina, and V. A. Kargin

The L. Ya. Karpov Physicochemical Institute, USSR

It has been shown[1–4] that under certain conditions it is possible to obtain globular structures from ordinary linear polymers. Globulization of the molecules in these cases was induced by formation of intramolecular bonds between active groups which were either present in the molecular chains or were introduced into them in various ways. Globular structures of certain proteins, gelatin, casein and synthetic and natural rubbers were obtained. In a number of properties, namely: solubility, solution viscosity, mechanical properties of films and others, the polymers with "globular" molecular structure differed considerably from the original polymers, evidently because of the difference in the molecular form.

The degree of globulization was determined[1–4] mainly by measurement of solution viscosity. It is known, however, that changes in the composition of the medium also produce changes of solution viscosity in some instances. For example, alcohols are often used in the rubber industry for decreasing the viscosity of rubber adhesives. On the supposition that coiling of the molecules also takes place when nonsolvents are added to rubber solutions, we commenced an investigation of this effect. This study was also of interest because there is a significant difference between globulization of rubber caused by addition of active substances to solutions, and that caused by addition of nonsolvents. In the former case coiling of the molecules is largely the consequence of energy interaction, while in the latter globulization is determined by entropy effects.

The present communication contains data obtained in a study of the influence of added nonsolvents on the viscosity of solutions of different rubbers. The materials studied were natural smoked sheet rubber and synthetic rubbers, mainly of the sodium butadiene type. The solvent used was carbon tetrachloride, and the nonsolvent was methyl alcohol. The degree of globulization of the molecules was determined, as previously, by measurements of solution viscosity. Rubber solutions of different concentrations were used in the experiments.

The experimental results are shown in Figure 1, where the amounts of methyl alcohol or CCl_4 in milliliters added to 5 ml of the solution (Curves *1* and *3*) and the time, Curve *2* (the time is taken from the moment of addition of bromine to the solution; the amount of bromine taken corresponded to 10% of the unsaturated bond content in the rubber) are taken along the abscissa axis and the specific viscosity along the ordinate axis; it is seen that the viscosity decrease of the rubber solutions is proportional to the amount of nonsolvent (methyl alcohol) added, right up to precipitation of the rubber. The limiting value of the viscosity of rubber solutions in presence of the nonsolvent differs little from the viscosity of globular rubber solutions produced by bromination.

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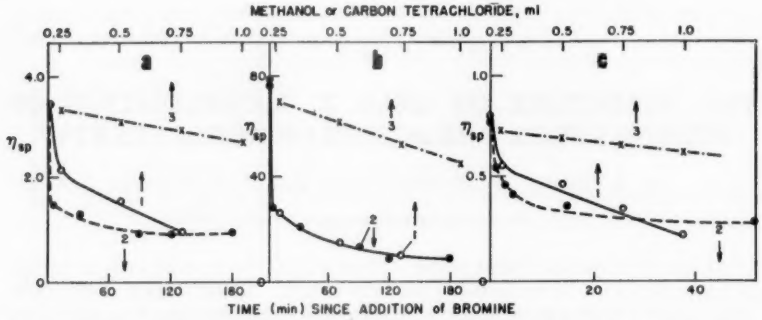

FIG. 1.—Effects on the viscosity of 0.25% NR solution (*a*), 1% NR solution (*b*), and 0.25% SK-B solution (*c*), of addition of: *1*) methyl alcohol; *2*) 10% of bromine; *3*) carbon tetrachloride.

Experiments were carried out to determine the effects of rubber solution concentration and temperature on the amount of methyl alcohol required to produce turbidity of the solution. The results show that the amount of methyl alcohol depends to some extent on the solution concentration (Table I) and to a large extent on the temperature (Figure 2). Figure 2 gives curves for the viscosity variations of 0.5% solution of natural rubber (of a low degree of milling) in carbon tetrachloride on addition of methyl alcohol. The curves in Figure 2 correspond to experimental temperatures of 0, 25 and 50°. The amounts of methyl alcohol in milliliters added to 5 ml of rubber solution are taken along the abscissa axis, and the specific viscosity of the solution along the ordinate axis. Arrows indicate precipitation of the rubber. Figure 2 shows that one and a half times more methyl alcohol is needed at 50° than at 0° to precipitate the rubber.

In dilute solutions (0.16%) of a number of rubbers precipitation of rubber occurs at practically the same contents of methyl alcohol. The only exception is polyisobutylene, which is precipitated at a lower alcohol content than the other rubbers (Table II).

It may be concluded from these results that globulization of rubbers by addition to the solutions of active substances which react with the rubber molecules (S_2Cl_2 and halogens) and the coiling of rubber molecules by the action of added nonsolvents have the common feature that in both cases the macromolecules assume a globular configuration. Experiments carried out in order to study the kinetics of globulization of the molecules caused by additions of non-

TABLE I

VARIATION OF THE AMOUNT OF CH_3OH IN MILLILITERS REQUIRED TO PRODUCE TURBIDITY, WITH THE CONCENTRATION OF THE RUBBER SOLUTION

Concentration of NR solution in %	0.1	0.16	0.25	0.4
Specific viscosity of solution	0.68	0.77	2.73	6.77
Amount of CH_3OH in ml to produce turbidity in 5 ml of solution	1.14	1.07	0.52	0.39

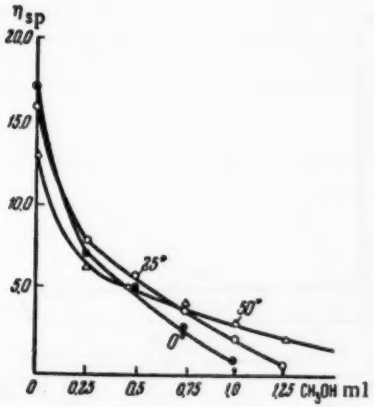

FIG. 2.—Effect of additions of methyl alcohol on the viscosity of 0.5% NR solution in CCl_4 at various temperatures.

solvents to the rubber solutions showed that on addition of methyl alcohol the viscosity of the rubber solutions falls almost instantaneously and remains constant for a considerable time. In contrast to this, globulization of rubber effected by the action of 20% of bromine (calculated on the unsaturated bonds) is clearly seen to be a function of time (Figure 3).

The following experiments were carried out to investigate the reversability of the globulization of rubber molecules caused by addition of nonsolvents to solutions. Methyl alcohol was added to a rubber solution the viscosity of which had been determined previously, and after thorough stirring the viscosity was measured again. The solvent was then removed from the mixture at room temperature by means of a vacuum pump. The residual rubber was dissolved in the pure solvent (CCl_4) and the viscosity of the solution was again measured. A comparison of the viscosity of this solution with the viscosity of the original rubber solution before addition of the methyl alcohol gave an indication of the reversibility of the globulization of the rubber molecules caused by addition of the nonsolvent. To allow for the influence of other factors (oxidation, etc.) on the viscosity of the rubber solution, a control experiment was carried out, which differed from the main experiment only by the addition of the same amount of

TABLE II

AMOUNTS OF CH_3OH IN ML CAUSING TURBIDITY IN 5 ML OF 0.16% RUBBER SOLUTIONS

Type of rubber	Amount of CH_3OH in ml	Type of rubber	Amount of CH_3OH in ml
Butyl rubber	1.25	Low-temperature No. 3	1.20
Low-temperature No. 1	1.25	SKS-30A	1.20
SK-B	1.30	Polyisobutylene	0.75
Isoprene	1.25	Neoprene	1.10
SK-B No. 1, low-temperature	1.30	NR, low mastication	1.10
SK-B No. 3, high-temperature	1.25		

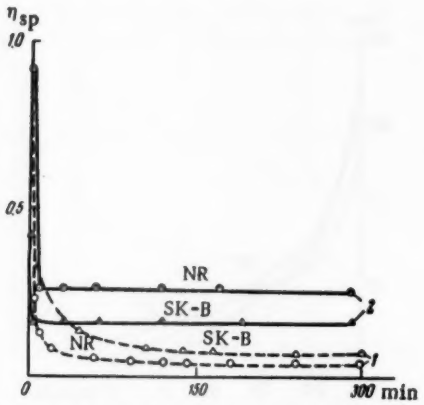

FIG. 3.—Effect of additions of bromine (*1*) and methyl alcohol (*2*) on the viscosities of 0.16% solutions of NR and SK-B.

pure solvent (CCl_4) instead of methyl alcohol to the rubber solution. The results of these experiments showed that even on incomplete evaporation of the rubber solution containing methyl alcohol, followed by dilution of the resultant concentrated solution with pure solvent (CCl_4) to the original concentration, the viscosity of the solution increases. Complete removal of the solvent followed by solution of the rubber in CCl_4 results in a greater viscosity increase (Table III).

It seemed possible that in consequence of the globulizing action of methyl alcohol on the rubber molecules the solubility of rubber in a mixture of CCl_4 and CH_3OH should differ from the solubility in pure CCl_4. Experiments showed that different rubbers dissolve much more rapidly in a mixture of CCl_4 and CH_3OH than in pure CCl_4. The viscosities of solutions of rubbers in the mixture are much lower than the viscosities of solutions in the pure solvent. For example, a 2.5% solution of NR (of a low degree of mastication) in CCl_4 is a nonfluid gelatinous mass, while a 2.5% solution of the same rubber in a mixture of CCl_4 and CH_3OH in 6.7 : 1 ratio is quite fluid, although viscous. An interesting feature is that, in contrast to solution in the pure solvent, solution of rubber in the solvent-nonsolvent mixture proceeds almost without swelling, which, naturally, is associated with globulization of the molecules.

TABLE III

EFFECT OF ADDITIONS OF CH_3OH AND CCl_4 ON THE SPECIFIC VISCOSITY OF RUBBER SOLUTIONS

Concentration of original NR solution in %	Specific viscosity			
	Of original solution	After addition to 10 ml of the original solution, of 15 ml of		After evaporation of mixture and solution of rubber in CCl_4
		CH_3OH	CCl_4	
0.4	6.95	1.9	—	5.2
0.4	6.95	—	5.3	5.0
1	70.6	9.0	—	32.3
1	70.6	—	42.0	38.0

If a low-viscosity solution of rubber containing methyl alcohol is evaporated and the rubber residue is then dissolved in pure CCl_4, the viscosity of the solution so formed differs little from the viscosity of a rubber solution of the same concentration, prepared without the use of methyl alcohol (Table IV).

TABLE IV

REVERSIBILITY OF THE GLOBULIZATION OF RUBBER MOLECULES

Composition of solvent	Specific viscosities of rubber solutions: 1% NR, Before evaporation	1% NR, After evaporation and solution in CCl_4	1% SKB, Before evaporation	1% SKB, After evaporation and solution in CCl_4	2.5% SKB, Before evaporation	2.5% SKB, After evaporation and solution in CCl_4
CCl_4	52.3	68.3	4.1	4.0	20.4	16.8
CCl_4:CH_3OH = 20:1	31.7	66.1	—	—	—	—
CCl_4:CH_3OH = 10:1	25.2	63.7	—	—	—	—
CCl_4:CH_3OH = 6.7:1	18.1	60.3	2.1	3.5	9.1	16.1

SUMMARY

1. Addition of nonsolvents to rubber solutions causes globulization of the macromolecules, similar to that occurring on addition of active substances (sulfur monochloride, halogens, etc.) to rubber solutions.

2. The difference between these processes lies in the fact that the coiling of the rubber molecues under the action of methyl alcohol is very rapid.

3. The globular structures in rubbers, produced by addition of nonsolvents to the solutions, in contrast to the stable globules formed in halogenation and vulcanization of rubber solution, are easily broken down and the molecules assume the linear form characteristic of the original rubber.

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VULCANIZATES FROM NATURAL RUBBER AND BIS-AZO COMPOUNDS. AGING PROPERTIES *

HEINZ ESSER

FARBENFABRIKEN BAYER AG, LEVERKUSEN, GERMANY

PREVIOUS WORK

In recent times, a number of publications by English, American, Russian, and German authors have appeared which describe the reactions of mono- and polyazo compounds with olefin systems. According to Alder, Pascher, and Schmitz[1], azodiformic acid (or azodicarboxylic acid) diethylester reacts with unsaturated hydrocarbons, such as, isobutylene, diisobutylene, and amylene, by "substituting addition in the allyl position" at the α-methylene group; a hydrogen shift takes place and N-alkenyl hydrazodiformic esters are formed according to the following reaction scheme:

$$H_2C{-}CH{=}CH_2 + ROOC{\cdot}N{=}N{\cdot}COOR \longrightarrow ROOC{-}NH{-}\underset{\displaystyle CH_2{-}CH{=}CH_2}{\overset{\displaystyle |}{N}}{-}COOR$$

Continuation of this work with bifunctional bis-azo compounds by E. Müller, S. Peterson, and O. Bayer during the war years led to several patent applications. It was found that in reaction of such bis-azo compounds with natural rubber or other rubbery compounds (polymers of butadiene or copolymers of butadiene and other hydrocarbons), a crosslinking reaction takes place between two hydrocarbon chains and the respective bis-azo compound. The question whether in this case a "direct" or "indirect substituting addition in the allylic position" takes place, remains open. These two types of reaction are thoroughly discussed in a publication of Alder, Söll and Söll[2]. Müller, Peterson, and Bayer[3] described their experiment in a short paper.

Rabjohn[4] as well as Flory, Rabjohn, and Schaffer[5,6] reported in 1948 and 1949, in several publications, the preparation of bis-azoesters and their use as vulcanizing agents. They found that natural rubber and GR-S type rubber can be vulcanized to different degrees of crosslinking; these vulcanizates do not differ greatly in their mechanical properties from sulfur vulcanizates. They found that when azodicarboxylic ester has reacted with bis-azo ester vulcanizates and 7% of the isoprene residues have branches through addition of the azo dicarboxylate, the tensile strength of the bis-azoester vulcanizate is reduced only very slightly.

Farmer and coworkers[7,8,9] also investigated the reactivity of alpha-methylene groups in olefinic hydrocarbons and their vulcanization. According to Farmer, reaction occurs also at the alpha-methylene group when maleic anhydride, maleic ester, peroxides, quinones, sulfur, lead tetra-acetate, selenium dioxide, or ozone interacts with olefins.

Interest in rubber vulcanization with bis-azoesters was revived by Ivanov[10]

* Translated by Otto C. Elmer for RUBBER CHEMISTRY & TECHNOLOGY from *Kautschuk und Gummi*, Vol. 11, pages WT 57–62 (1958); the author thanks Dr. Th. Kempermann for supporting this work and for performing a large part of the experimental work.

in 1956. The quantitative reaction of azo-dicarboxylic esters, respectively, bis-azodicarboxylic esters with natural rubber with formation of branches and cross-linking was confirmed. According to Ivanov, the properties of the bis-azocarboxylic ester vulcanizates with branches (formed with azo-dicarboxylic diethylester) vary appreciably from the bis-azoester vulcanizates that contain no branching. This is in contrast with the findings of Flory and coworkers. In addition, according to Ivanov's investigations, vulcanizates of natural rubber with bis-azoester show properties different from those of sulfur vulcanizates.

We, too, have looked into the vulcanization of natural rubber with bis-azo compounds. Our primary interest was the aging properties of such vulcanizates. It is known that sulfur, the classical vulcanizing agent, has a deleterious effect on the aging properties of natural and synthetic rubber vulcanizates. There is, therefore, no lack of attempts to replace the sulfur with a similarly acting vulcanizing agent that might give better aging properties. We may mention selenium, tellurium, and their halogen compounds, peroxides, disulfides, isocyanates, and isothiocyanates, quinonedioxime, and dibenzoquinonedioxime, phenols, amines, aromatic nitro compounds, Grignard compounds, tetraalkylthiuram disulfides, reactive phenol formaldehyde resins and others. Sulfur has remained the universal and classical vulcanizing agent, though one or another vulcanizing agent has found a certain amount of industrial use.

THIS INVESTIGATION

All workers to date have used solutions rather than solid rubber mixtures. Thus Flory and Ivanov worked with vulcanizates that were prepared by casting a natural rubber solution containing a bis-azoester onto a glass plate, evaporating the solvent and heating of the film. To meet practical requirements, we chose loaded solid rubber mixtures to which we added the respective bis-azo compound on the rubber mill. The aim of our investigation was the study of the vulcanization process of natural rubber with bis-azo compounds and to study the aging of such mixtures.

It soon developed that bis-azo esters with aliphatic substituents on each side of their —N=N— groups were so reactive that vulcanization occurred with many mixtures even on the mill. Because of the uncertainties in processing caused by these poor scorch properties, we had to search for other bis-azo compounds. We believed that bis-azo compounds in which the azo groups were flanked on one side by an aromatic radical would be less reactive because of resonance in the —N=N—Ph system and also because of stearic effects; the reactivity should be reduced to a point where one could obtain satisfactory processing. We found in hexamethylene-1,6-bis(phenyl-azomonocarbonamide) (BAA, II) a suitable compound. Such compounds are obtainable without difficulty through the reaction of a diisocyanate and a monosubstituted hydrazine and subsequent oxidation of the bis-hydrazo compound; they were first prepared by Müller and coworkers[3]. We condensed a toluene solution of hexamethylene-1,6-diisocyanate and phenylhydrazine. The resulting bis-hydrazo compound (I) may be oxidized by known methods to the bis-azo compound:

$$\mathrm{OCN(CH_2)_6NCO}$$

$$+\downarrow 2\ \mathrm{C_6H_5NHNH_2}$$

$$\mathrm{C_6H_5HN{-}HNOCNH(CH_2)_6NHCONH{-}NHC_6H_5} \qquad \text{BHA (I)}$$

$$+\downarrow \mathrm{O_2}$$

$$\mathrm{C_6H_5N{=}NOCNH(CH_2)_6NHCON{=}NC_6H_5} \qquad \text{BAA (II)}$$

VULCANIZATION WITH BIS-AZO COMPOUNDS

The tightening and accelerating action of BAA.—We used for our first experiment a white mixture of the composition:

COMPOSITION OF MIXTURE A

Pale crepe	100.0
Stearic acid	1.0
Vulkacit Thiuram (TMTD)	0.2
Vulkacit DM (MBTS)	0.2
Zinc white Rotsiegel	5.0
Titanium dioxide	4.0
Blanc fixe	10.0

Increasing amounts of BAA were added to this mixture with constant sulfur dosage as shown in Figure 1 to determine the effect of BAA on the modulus of the mixture. It is found that with increasing BAA, a continuously rising modulus is obtained. It is striking that all mixtures containing BAA begin to vulcanize much earlier. This fact makes the question reasonable whether the vulcanization with BAA is only an accelerator-effect and not a true crosslinking reaction. Later observations seem to support this assumption. We have investigated this question thoroughly and will consider it again in a later section.

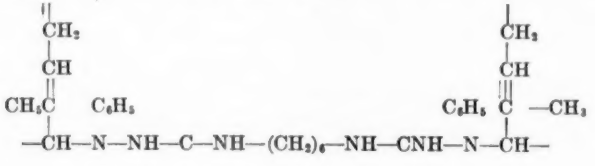
The role of sulfur in the vulcanization of BAA-containing mixtures.—In another white mixture B, the amount of sulfur was steadily reduced while the amount of BAA was increased. This should determine if it is possible to work without sulfur and also the optimum sulfur to BAA ratio. We found that even at very high BAA content (6%), it was not possible to eliminate sulfur completely. This fact also leaves the possibility open that BAA has only accelerating properties. Details are given in Figure 2. A sulfur:BAA ratio of 1:1.7 . . . 2 was advantageous.

COMPOSITION OF MIXTURE B

Pale crepe	100.0
Stearic acid	1.0
Zinc white Rotsiegel	10.0
Blanc fixe	60.0
Titanium dixoide	10.0
Vulkacit Thiuram MS (TMTM)	0.5

The role of accelerators in the vulcanization of BAA-containing mixtures.—In Mixture B, the amount of Vulkacit MS was steadily reduced while the amount of sulfur and BAA remained constant. Thereby, it was shown that the accelerator could be reduced in concentration but not completely eliminated (Figure 3). This behavior seems to indicate that BAA does not, or at least not exclusively, act as an accelerator.

If one assumes that BAA primarily adds to two rubber chains because of the two azo groups, there is formed a substituted bis-hydrazo crosslink through substituting addition with hydrogen migration:



It certainly seems plausible that these newly formed hydrazo groups, which could be looked upon as ureas or semicarbazides, would have accelerator properties. Furthermore, the bis-azo compound itself as carbonamide could have accelerating action.

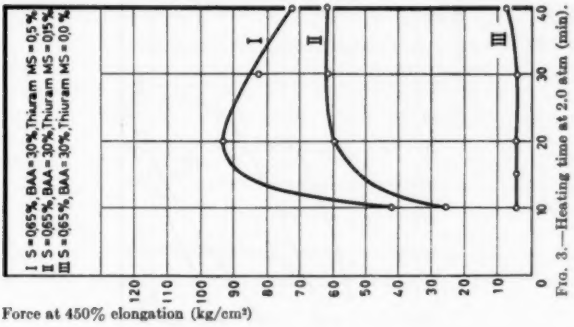

I S = 0.65%, BAA = 30%, Thiuram MS = 0.5 %
II S = 0.65%, BAA = 30%, Thiuram MS = 0.15 %
III S = 0.65%, BAA = 30%, Thiuram MS = 0.0 %
I
II
III
120 110 100 90 80 70 60 50 40 30 20 10
0 10 20 30 40
Force at 450% elongation (kg/cm²)
Heating time at 2.0 atm (min).

FIG. 3.—Heating time at 2.0 atm (min).

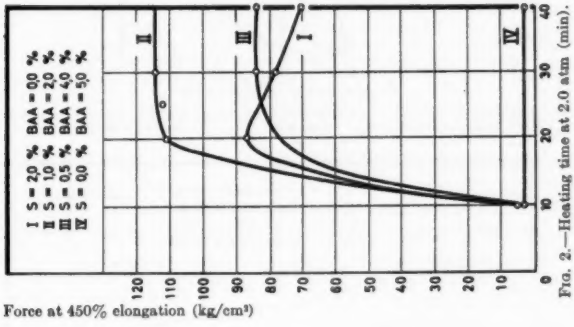

I S = 2.0 % BAA = 0.0 %
II S = 1.0 % BAA = 2.0 %
III S = 0.5 % BAA = 4.0 %
IV S = 0.0 % BAA = 5.0 %
II
III
I
IV
120 110 100 90 80 70 60 50 40 30 20 10
0 10 20 30 40
Force at 450% elongation (kg/cm²)
Heating time at 2.0 atm (min).

FIG. 2.—Heating time at 2.0 atm (min).

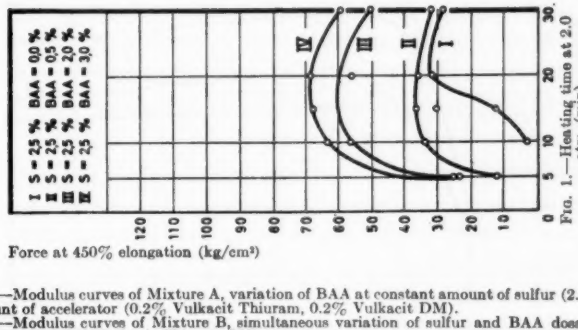

I S = 2.5 % BAA = 0.0 %
II S = 2.5 % BAA = 0.5 %
III S = 2.5 % BAA = 2.0 %
IV S = 2.5 % BAA = 3.0 %
IV
III
II
I
120 110 100 90 80 70 60 50 40 30 20 10
0 5 10 20 30
Force at 450% elongation (kg/cm²)
Heating time at 2.0 atm (min).

FIG. 1.—Heating time at 2.0 atm (min).

FIG. 1.—Modulus curves of Mixture A, variation of BAA at constant amount of sulfur (2.5%) and constant amount of accelerator (0.2% Vulkacit Thiuram, 0.2% Vulkacit DM).

FIG. 2.—Modulus curves of Mixture B, simultaneous variation of sulfur and BAA dosage with constant accelerator (0.5% Vulkacit Thiuram MS).

FIG. 3.—Modulus curves of Mixture B, variation of accelerator with constant amount of sulfur (0.65% sulfur, 3% BAA).

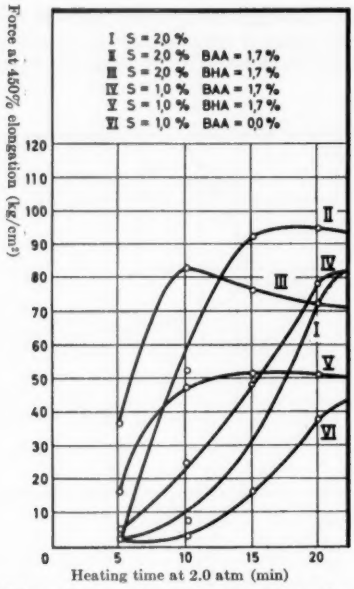

I S = 2,0 %
II S = 2,0 % BAA = 1,7 %
III S = 2,0 % BHA = 1,7 %
IV S = 1,0 % BAA = 1,7 %
V S = 1,0 % BHA = 1,7 %
VI S = 1,0 % BAA = 0,0 %
Force at 450% elongation (kg/cm²)
Heating time at 2.0 atm (min)

FIG. 4.—Modulus curves of Mixture B, comparison of the accelerating and crosslinking action of BAA and BHA with constant level of accelerator (0.5% Vulkacit Thiuram MS).

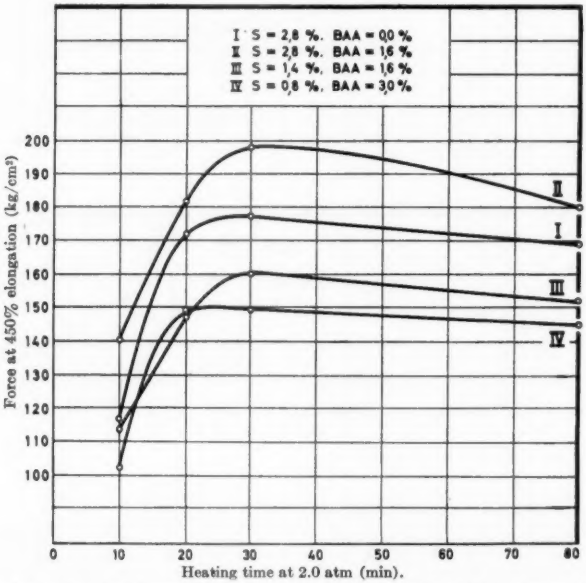


FIG. 5.—Modulus curves for Mixture C_1, simultaneous variation of sulfur and BAA dosage with constant amount of accelerator (0.6% Vulkacit CZ) in a carbon black mixture.

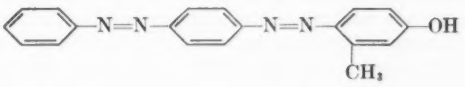
Comparison of BAA with BHA with regard to their accelerating properties.—To obtain a final picture of the action and influence of BAA on the vulcanization, we have compared the basic bis-hydrazo compound BHA with BAA in Mixture B. It is clearly shown that BHA accelerates the vulcanization but does not contribute to crosslinking and increasing of the modulus. If one looks at modulus curve I in Figure 4 of the BHA-free mixture and compares it with III of the BHA-containing mixture, one finds the vulcanization optimum approximately at the same modulus. The BAA-containing mixture shows in modulus curve II that a higher modulus appears as well as an earlier vulcanization; it acts, therefore, as a crosslinking vulcanizing agent and as accelerator activator.

Experiment with a mixture of natural rubber and carbon black.—The tightening action of BAA is less obvious in the black-containing mixture C than in the nonblack mixtures. However, the effect is still clearly noticeable through the increased modulus. It is also evident from the values in the early part of the vulcanization (Figure 5) that BAA is acting as accelerator and vulcanization agent simultaneously.

Composition of Test-Mixture C

Sheets, Defo 1000	100.0
Pine tar	2.5
Zinc white Rotsiegel	3.0
Black CK-3	45.0
Stearic acid	3.0
Phenyl-1-naphthylamine	1.5
Phenylcyclohexyl-*p*-phenylene diamine	0.7
Vulkacit CZ (Santocure)	0.6

Experiments with bis-azo compounds substituted on both sides with an aromatic nucleus.—To round out our vulcanization studies, we investigated, finally, a bis-azo compound substituted on both sides of the azo group with an aromatic nucleus, 4-phenylazo-4′-hydroxy-2′-methyl-azobenzene. The reactivity of this



(III)

compound is so low that in Mixture B together with 2.5 parts of sulfur no crosslinking effect was observed. Summarizing the results obtained for the vulcanization with bis-azo compounds, we can state:

a. Bis-azo esters have vulcanization action in the absence of sulfur when used in rubber-solution as was shown from the work of Rabjohn[4], Flory[5,6] and Ivanov[10]. In solvent-free rubber mixtures, in the presence of sulfur and accelerators, the vulcanization action becomes so fast that crosslinking occurs on the mill during mixing.

b. Hexamethylene-1,6-bis(phenyl-azomonocarbonamide) (II, BAA) gave perfectly satisfactory mill-mixing because of its decreased reactivity. In white mixtures it increases the modulus very much in the presence of sulfur and accelerators, and markedly in carbon black mixtures, while the vulcanization process in both cases was clearly accelerated. This latter effect may be favored partly by the carbonamide groups present in BAA and partly by the BAA/rubber adduct urea or semicarbazide groups. The complicated reaction mechanism of the vulcanization system sulfur-BAA-accelerator has not been clarified in its details and goes beyond the scope of the present work.

c. The bis-hydrazo compound BHA (I) from which BAA is prepared, shows definite accelerator action but, as expected, no crosslinking action.

d. The exclusively aromatic compound (III) shows neither vulcanizing nor accelerating action even in the presence of sulfur and accelerators.

AGING EXPERIMENTS WITH BAA-CONTAINING VULCANIZATES

We extended our aging experiments to include rapid tests that have attracted much attention lately; this should give us the largest possible basis and an accurate picture of the aging of bis-azo vulcanizates. We observed among others the relaxation and creep properties as well as oxygen absorption. In these experiments, Mixture A was used.

Oxygen absorption.—A carefully powdered sample of vulcanizate is heated to 100° C, its oxygen absorption measured volumetrically and reduced to standard conditions. If one plots the volume against time, one obtains in the region of small oxygen absorption approximately a straight line. The slope of this line is a measure of the ease of oxidation.

TABLE I

OXYGEN ABSORPTION OF VULCANIZATES OF MIXTURE A AT 100° C WITH VARYING BAA AND SULFUR DOSAGE

	Comparison mixture with 2.5 S*	1.0** BAA 2.5 S	0.5 BAA 2.5 S	1.0 BAA 2.5 S	2.0 BAA 2.5 S	2.0 BAA 1.3 S	3.3 BAA 0.65 S
$\frac{cm^2}{g \cdot hr} O_2$	1.0	0.29	0.46	0.37	0.35	0.26	0.23

* Calculated on 100 parts of rubber.
** 2,2'-methylene-bis-(4-methyl-6-*tert*-butylphenol).

The antixoidants and sulfur, respectively BAA and sulfur given in Table I, were added to the white mixture A. As one can see from the table, the values obtained from BAA containing mixtures are good; they are comparable with those obtained from a mixture containing the commercial antioxidant 2,2'-methylene-bis-(4-methyl-6-*tert*-butylphenol). It is interesting that less oxygen is absorbed with increasing BAA and decreasing sulfur dosage; that is, aging is improved in that direction.

Creep test.—In this rapid test, a ring-shaped rubber sample is stretched under constant load (in our case 6.4 kg/cm²). The rubber sample as well as the complete apparatus are placed in a constant temperature cabinet (in our case 105° C) that is equipped with air circulation. Oxidation processes in the rubber sample cause decrease in the number of crosslinking positions and slowly decreasing modulus, while elongation increases correspondingly. This increase in elongation is termed "creep". The creep is then given as[11,12]

$$D = \frac{l_t - l_0}{l_0}$$

where l_t = length of the stretched ring at time t
l_0 = length of the stretched ring at time $t = 0$

The length of the stretched ring at time $t = 0$ is determined by extrapolating. The aging in the creep test differs from the Geer aging in the hot air cabinet only by the fact that the sample is under tension during the oxidation.

TABLE II

CREEP-ELONGATION OF VULCANIZATES OF TEST-MIXTURE A IN % AT 105° C AFTER 5 HOURS WITH VARIATION OF BAA AND SULFUR DOSAGE

Amount antioxidant, or BAA+S	Comparison mixture with only 2.5 S	1.0* 2.5 S	0.5 BAA 2.5 S	1.0 BAA 2.5 S	2.0 BAA 2.5 S	3.3 BAA 2.5 S
Creep-elongation in % at 105° C after 5 hours (500 g load)	60	20	26	13.5	13.5	11.0

* 2,2'-methylene-bis (4-methyl-6-*tert*-butylphenol).

We used the same white mixture A for the creep test that we used in the oxygen absorption test. The values that were obtained are given in Table II. In this test, too, the BAA vulcanized samples give outstanding aging properties.

Relaxation test.—The test is based on the decrease in tension of a constant 150% elongated ring in the hot air cabinet at 110° C. The load in this test is varied by changing of weights; a constant elongation is assured by this method. The aging is characterized through the quantity R that is calculated as follows:

$$R = \frac{P}{P_0} \cdot 100$$

where P = load at time t
P_0 = load at time $t = 0$
P_0 is calculated by extrapolation.

The same Mixture A was used in the relaxation test and good aging behavior was found for BAA vulcanizates (Table III).

Hot air aging.—For the hot air aging, the white mixture B was used with varying amounts of BAA and sulfur; this mixture was compared with a standard mixture that contained 2.0 parts sulfur and 1.0 part antioxidant (per 100.0 parts natural rubber). The ratio of BAA:sulfur was chosen to give approximately the same modulus and the same level of physical properties as the mixture containing antioxidant that was aged at the same time.

The good aging of BAA containing vulcanizates in the creep, relaxation, and oxygen absorption test, as well as the wide plateau in their physical properties, would point toward a good hot air aging. Our expectations were surpassed by the experimental results. Comparison mixtures containing proven antioxidants show, for example, on 14-day aging a decrease of tensile strength from ca. 190 kg/cm² to about 40 . . . 65 kg/cm², while the BAA containing vulcanizates retain a tensile of 100 . . . 120 kg/cm². The ratio of BAA:sulfur

TABLE III

RELAXATION-TEST OF VULCANIZATES OF TEST-MIXTURE A AT 110° C HOT AIR AND 150% ELONGATION AFTER 120 MIN WITH VARIATION OF BAA AND SULFUR DOSAGE

	Comparison mixture with only 2.5 S	1.0*	0.5 BAA 2.5 S	1.0 BAA 2.5 S	2.0 BAA 2.5 S	3.3 BAA 2.5 S	2.0 BAA 1.3 S	3.3 BAA 0.65 S
R in %	25	54.6	45.9	55.8	53.2	51.6	62.8	58.9

* 2,2'-Methylene-bis-(4-methyl-6-*tert*-butylphenol).

For Tables IV and V: F = Tensile strength, kg/cm²; D = Elongation, %; b.D = Permanent elongation, %; M300 = stress (modulus) at 300% elongation; M450 = stress (modulus) at 450% elongation; E 24° = rebound, % at 24° C; E 75° = rebound, % at 75° C; H 24° = hardness, ° Shore A at 24° C; Str = Structure, kg/cm².

TABLE IV

HOT AIR AGING OF MIXTURE B AT 100° C

Vulcanization at 2.00 atm	Sulfur =0.73% BAA =3.00%									Sulfur =1.00% BAA =1.70%									Sulfur =1.80% BAA =0.75%								
	F	D	b.D	M 300	M 450	E 24°	E 75°	H 24°	Str.	F	D	b.D	M 300	M 450	E 24°	E 75°	H 24°	Str.	F	D	b.D	M 300	M 450	E 24°	E 75°	H 24°	Str.
15 min	200	682	17	31	68	71	72	49	24	203	687	19	31	71	72	73	50	24	205	665	20	33	78	72	75	51	18
20 min	203	667	18	31	72	71	72	50	24	205	670	18	31	73	71	73	50	26	200	657	18	34	75	72	75	51	23
After 24 hours hot air aging at 100° C																											
	152	585	16	35	78	67	69	52	4	152	555	16	35	80	68	70	53	4	94	470	12	37	82	68	71	52	3
	152	560	15	35	80	68	70	52	4	138	550	14	37	80	69	70	53	5	91	470	12	36	81	68	72	52	3
After 48 hours hot air aging at 100° C																											
	130	555	12	35	74	66	70	50	5	124	520	11	35	79	66	70	50	5	58	370	6	36	—	68	71	51	4
	131	560	12	35	77	66	69	50	6	139	573	13	36	79	66	71	51	5	62	418	7	36	—	68	71	51	4
After 72 hours hot air aging at 100° C																											
	117	555	14	32	69	63	62	50	9	118	475	12	34	78	65	69	51	7	37	345	6	31	—	63	69	51	6
	113	555	13	32	69	62	66	51	10	123	530	14	35	79	65	70	51	7	54	415	7	31	—	63	69	51	5
After 96 hours hot air aging at 100° C																											
	105	550	17	29	63	60	66	50	—	109	530	15	33	76	63	69	50	—	31	305	5	—	—	61	67	50	—
	109	545	17	30	65	61	66	50	—	102	485	15	34	76	63	69	50	—	24	245	3	—	—	62	67	50	—
After 14 days hot air aging at 70° C																											
	165	560	18	40	75	70	71	58	—	174	580	17	42	72	71	72	54	15	133	475	2	52	88	70	72	56	7
	167	570	18	42	78	70	71	58	13	180	570	12	44	78	70	72	54	14	131	525	18	48	80	69	71	54	7

TABLE IV (*Cont.*)

Vulcanization at 2.00 atm	Sulfur = 2.00% [1] = 1.00%									Sulfur = 2.00% [2] = 1.00%									Sulfur = 2.00% [3] = 1.00%								
	F	D	b.D	M 300	M 450	E 24°	E 75°	H 24°	Str.	F	D	b.D	M 300	M 450	E 24°	E 75°	H 24°	Str.	F	D	b.D	M 300	M 450	E 24°	E 75°	H 24°	Str.
15 min	198	675	22	31	70	71	74	50	19	181	670	18	30	62	71	73	49	18	178	670	21	27	65	71	73	49	20
20 min	215	702	21	31	69	71	75	50	20	187	675	19	29	64	72	75	50	16	192	692	17	28	64	72	75	49	17
After 24 hours hot air aging at 100° C																											
	51	390	10	37	—	69	71	52	3	37	290	5	—	—	70	72	54	2	52	320	7	45	—	70	70	56	2
	88	477	12	35	80	68	72	52	4	88	455	11	40	—	70	72	54	3	99	450	12	46	99	72	74	56	3
After 48 hours hot air aging at 100° C																											
	39	320	3	35	—	67	72	51	4	37	295	3	—	—	68	71	52	3	54	325	5	47	—	72	73	55	3
	74	450	9	34	—	66	70	51	4	54	355	4	39	—	69	72	51	4	34	280	3	—	—	72	74	55	6
After 72 hours hot air aging at 100° C																											
	30	295	3	31	—	65	69	51	7	28	235	2	—	—	67	70	55	4	42	325	6	—	—	70	71	65	5
	42	385	5	31	—	63	69	50	5	34	305	4	33	—	66	71	51	4	59	370	8	42	—	70	73	55	4
After 96 hours hot air aging at 100° C																											
	19	210	3	—	—	61	67	50	—	27	255	3	—	—	65	69	51	—	28	210	2	—	—	69	72	55	—
	26	260	5	—	—	61	65	60	—	28	255	2	—	—	64	70	51	—	38	275	4	—	—	70	72	55	—

[1] 2,2′-Methylene-*bis*-(4-methyl-6-cyclohexylphenol).
[2] 2,2′-Methylene-*bis*-(4-methyl-6-*tert*-butylphenol).
[3] N-Cyclohexyl-N′-phenyl-*p*-phenylenediamine.

of 1.7 : 1 proved particularly good in hot air aging. Table IV and Figure 6 show the values found.

Aging in the oxygen bomb.—We subjected our vulcanizates to aging in the oxygen bomb at 70° C and 21 atm. Vulcanizates made from Mixture B, the same as in the hot air aging, were tested. The BAA containing vulcanizates showed a poorer aging behavior in the oxygen bomb than in the other aging tests. The physical properties of BAA containing vulcanizates, after six days of bomb aging, still remain comparable to those found in vulcanizates containing proven antioxidants; after the ninth day of aging, a softening and subse-

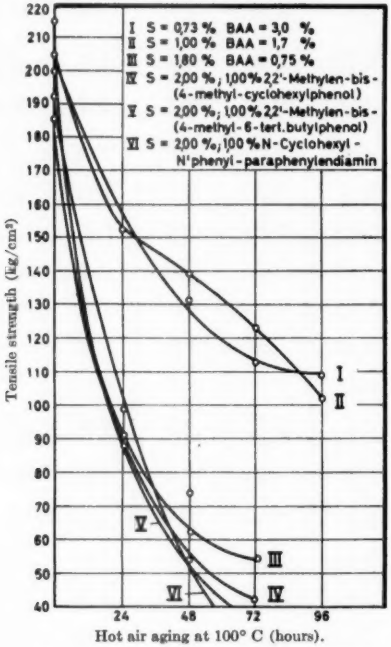

I S = 0,73 % BAA = 3,0 %
II S = 1,00 % BAA = 1,7 %
III S = 1,80 % BAA = 0,75 %
IV S = 2,00 %; 1,00 % 2,2'-Methylen-bis-(4-methyl-cyclohexylphenol)
V S = 2,00 %; 1,00 % 2,2'-Methylen-bis-(4-methyl-6-tert.butylphenol)
VI S = 2,00 %; 1,00 % N-Cyclohexyl-N'phenyl-paraphenylendiamin
Tensile strength (kg/cm²)
Hot air aging at 100° C (hours).

FIG. 6.—Hot air aging of Mixture B at 100° C.

quent embrittlement occurs, and after 11 days the BAA containing test specimens would not even reach 50 kg/cm² tensile strength. This phenomenon may be explained by the possibility that C–N bonds formed during the crosslinking of BAA with the natural rubber chains and could be attacked and broken by the continuous action of oxygen. The results in the oxygen bomb are not surprising, if one considers the higher stability of the C–C bond compared with the C—N bond (Table V and Figure 7).

SUMMARY

Nonblack as well as black loaded natural rubber compounds were vulcanized by addition of hexamethylene-1,6-bis(phenyl-azomonocarbonamide) (BAA).

TABLE V

AGING OF MIXTURE B IN OXYGEN BOMB AT 70° C AND 21 ATM

Vulcanization at 2.00 atm	Sulfur = 0.73%, BAA = 3.00%									Sulfur = 1.00%, BAA = 1.70%									Sulfur = 1.80%, BAA = 0.75%								
	F	D	b.D	M 300	M 450	E 24°	E 75°	H	Str.	F	D	b.D	M 300	M 450	E 24°	E 75°	H	Str.	F	D	b.D	M 300	M 450	E 24°	E 75°	H	Str.
After 6 days aging in oxygen bomb at 70° C																											
15 min	107	545	17	31	64	59	56	47	6	124	590	21	34	71	57	56	48	8	84	450	23	37	70	53	56	60	8
20 min	108	500	15	33	67	58	57	47	7	109	565	20	36	71	58	56	48	7	40	295	9	—	—	40	46	50	9
After 11 days aging in oxygen bomb at 70° C all samples destroyed																											
	Sulfur = 2.00%, [1] = 1.00%									Sulfur = 2.00%, [2] = 1.00%									Sulfur = 2.00%, [3] = 1.00%								
	F	D	b.D	M 300	M 450	E 24°	E 75°	H	Str.	F	D	b.D	M 300	M 450	E 24°	E 75°	H	Str.	F	D	b.D	M 300	M 450	E 24°	E 75°	H	Str.
After 6 days aging in the oxygen bomb at 70° C																											
	128	500	16	45	—	68	66	53	9	113	465	10	50	105	70	71	55	5.5	138	510	14	49	100	71	70	54	6
	124	515	17	36	78	65	67	50	7	133	530	15	40	89	70	72	53	7.5	146	555	20	41	89	69	70	53	9
After 11 days aging in the oxygen bomb at 70° C																											
	85	445	11	42	—	61	67	51	4	62	345	6	50	—	66	70	55	3.5	65	380	10	47	—	66	70	54	5.5
	105	515	14	37	76	59	66	50	5	109	500	15	40	87	65	70	54	6.5	112	510	15	34	84	65	69	52	6

[1] 2,2′-Methylene-*bis*-(4-methyl-5-cyclohexylphenol).
[2] 2,2′-Methylene-*bis*-(4-methyl-6-*tert*-butylphenol).
[3] N-Cyclohexyl-N′-phenyl-*p*-phenylenediamine.

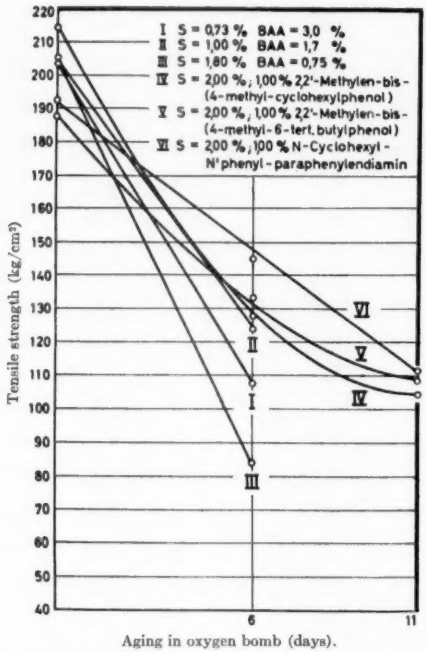


FIG. 7.—Aging of Mixture B in the oxygen bomb at 70° C and 21 atm.

The accelerating and vulcanizing action of BAA is discussed on the basis of modulus curves. The experiments show that BAA alone is not active as a vulcanizing agent. To achieve good vulcanization, sulfur is also needed; the optimum sulfur level is much lower than in normal compounds. Furthermore, it is shown that BAA compounds need addition of an accelerator. Aging stability of BAA vulcanizates was tested by modern rapid tests (relaxation, creep, and oxygen absorption) as well as by classical methods (hot air and oxygen bomb aging). Vulcanization in which BAA was substituted for part of the sulfur showed excellent aging, comparable only with thiuram vulcanizates in the rapid tests and in hot air aging; aging in the oxygen bomb gave only fair results.

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THE PHOTOVULCANIZATION OF BUTYL AND SKB (POLYBUTADIENE) RUBBERS *

YU. S. ZUEV

It is known that the mechanical properties of raw and vulcanized rubbers change markedly under the action of light in which not only oxidation processes but also photovulcanization processes in which sulfur is involved[1] play an essential part.

In view of the wide interest shown lately in questions of radiation vulcanization[2] of polymers[3], as well as the possibility of reducing the photodegradation effect upon the mechanical properties of some polymers, we made studies of the photovulcanization of butyl rubber (degradation by irradiation) and SKB (polybutadiene) rubber (structure formation by irradiation).

The study was made on films 200μ thick of purified butyl rubber with a molecular weight of about 42,000 and an unsaturation[4] of about 1%. Both ordinary (twice crystallized) sulfur and radioactive S^{35} were used.

The films obtained from a solution of rubber plus sulfur on cellophane were irradiated with a PRK-7 lamp through a Pyrex glass light filter and distilled water at a distance of 25 cm. Then determinations were made of the absorption spectrum and the static modulus[5] 30 minutes and 24 hours after applying the load. The amount of free sulfur remaining in samples extracted previously was determined from the intensity of the S^{35} radiation.

SKB not containing PBNA was reprecipitated from a benzene solution. When films of SKB (200μ thick) were irradiated, the light filters UFS-1, ZhS-4 and OS-5 were used[6]. After the irradiation of the SKB films their static modulus was determined 30 minutes after the application of the load.

When we irradiated butyl rubber containing 0.25 to 2.5% sulfur, we observed a distinct photovulcanization optimum (see Figure 1) in the modulus as a function of irradiation time[7] like that which occurs in thermal vulcanization[8], and an optimum of the photovulcanization rate as a function of sulfur concentration.

The nature of the optimum of modulus as a function of irradiation time.—One may assume that the sulfur combination process which accompanies structure formation in rubber takes place as a result of the light absorbed by the free sulfur (i.e., that with a wavelength $\lambda < 450$ mμ). We have shown that the light absorption increases to the degree that the sulfur is combined (thus where $\lambda = 450$ mμ, E increases from 0.1 to 2 after 30 hours' irradiation) and the absorption spectrum of the system extends up to the infrared region. The absorption of light by the sulfur compounds formed during photovulcanization brings about a degradation of the polymer. Hence the part played by degradation processes increases in proportion to the sulfur combination, because of the increase in the absorption of light, and the structure formation diminishes because of the disappearance of free sulfur. It is because of this also that an optimum appears in the modulus as a function of irradiation time. From this

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point of view it is seen that when a photovulcanizate is irradiated in a region below the optimum with light which has passed through a solution of sulfur in benzene (i.e., with light which contains no rays capable of bringing about structure formation), a degradation of the butyl rubber photovulcanizate takes place (Figure 1, Curve *5*).

It was interesting to verify whether degradation processes occur in the photovulcanization of SKB, which unlike butyl rubber shows structure formation under the action of light.

In the system SKB-sulfur the structure formation processes occur under the action of light by means of photovulcanization and photooxidation, as well as through the direct action of light on the rubber. These processes may mask the increase in the number of acts of degradation when the absorption capacity of the polymer increases during the photovulcanization process.

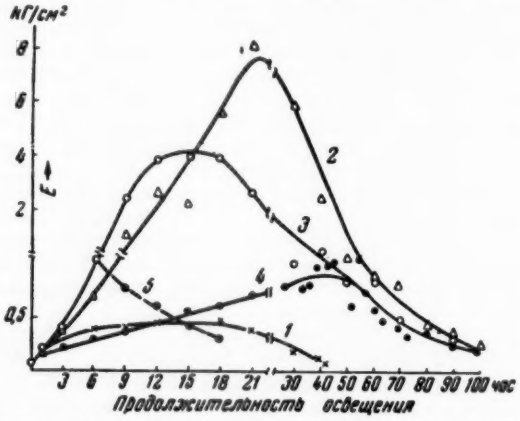

FIG. 1.—Kinetics of photovulcanization of butyl rubber. Sulfur content of rubber: *1*—0.25%; *2*—0.5%; *3*—1%; *4*—2.5%; *5*—Irradiated through a solution of sulfur in benzene. The abscissa represents time of irradiation, the ordinate the modulus in kg/cm².

In order to observe the photodegradation of SKB, the following experiment was set up. Films of SKB containing 0–2.5% sulfur were exposed to light through light filter UFS-1 (Figure 2) (transmitting in the 240–400 mμ wavelength region, absorbing the visible light which causes degradation) with the aim of weakening the degradation which takes place during photovulcanization. After 6 hours filter UFS-1 was replaced by light filter OS-5 (transmitting light with wavelengths $\lambda > 440$ mμ). The light passing through OS-5 should result mainly in a photodegradation of the vulcanizate.

As Figure 2 shows, in photovulcanizates containing 1% and 1.5% of their initial free sulfur, the degradation actually occurred[9]. This indicates the unstable nature of the sulfur bonds which were ruptured under the action of the visible light which they absorbed. The absence of photodegradation in the samples with 0.25% and 2.5% of their initial sulfur is explained by the fact that photovulcanization has proceeded at a fairly low rate in them (Curve *5* of Figure 2 differs hardly at all from Curve *1* for the sample without sulfur), and only a small amount of structures capable of rupturing under exposure to light has been formed.

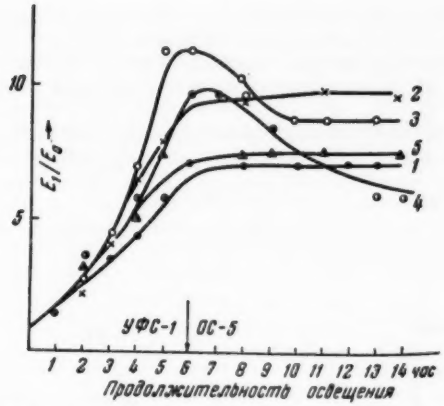

FIG. 2.—Kinetics of photovulcanization of SKB through UFS-1 and OS-5 light filters. Sulfur concentration: *1*—0%; *2*—0.25%; *3*—1%; *4*—1.5%; *5*—2.5%. The abscissa represents the duration of irradiation in hours, the ordinate the ratio of moduli E_1/E_0.

We have tried to determine whether the optimum photovulcanization of butyl rubber is related to the kinetics of sulfur combination and with the nature and mobility of the sulfur links. The kinetics of sulfur combination are shown in Figure 3. It is seen from these data that: (1) the major part of the sulfur is combined before the moment when the optimum is reached, but a slow combination of sulfur takes place even after the optimum (except for the case with 0.25% sulfur, in which the sulfur is completely combined at the moment when the optimum is reached); (2) the largest amount of sulfur combined was 0.4–0.5%. If we consider that all of the sulfur combines at the double bonds, and take into account that part of the double bonds of butyl rubber (out of an amount of about 1%) are consumed by oxidation, then the calculation shows that the sulfur links must be polysulfide ones. This is confirmed by the fact that boiling the butyl rubber photovulcanizates for a period of 200 hours with sodium sulfite removes 55–65% of the combined sulfur.

The mobility[10] of the combined sulfur increases in the vicinity of the optimum. A film of the extracted photovulcanizate (2.5% of the initial S^{35}, optimum 45 hours) is pressed against the same kind of films containing ordinary

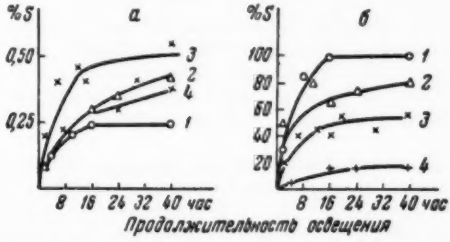

FIG. 3.—The kinetics of sulfur combination with butyl rubber during photovulcanization. a—The amount of combined sulfur in per cent of the rubber; b—the amount of combined sulfur in per cent of the sulfur incorporated. Concentration of sulfur: *1*—0.25%; *2*—0.5%; *3*—1%; *4*—2.5%.

sulfur, and heated at 130° C for 90 hours. As a result of this the photovulcanizate irradiated for 9, 16 and 25 hours exchanges about 30% of its sulfur, while the 40-hour photovulcanizate exchanges about 43%. This indicates an increase in the mobility of the combined sulfur when optimum vulcanization is approached.

The relation between optimum photovulcanization and sulfur concentration.—The optimum sulfur concentration for both butyl rubber and SKB was observed when they were irradiated through UFS-1. The nature of the relationship between concentration and photovulcanization, i.e., the acceleration of structure formation with an increase in sulfur concentration up to a certain value and the subsequent retardation of the process upon a further increase in

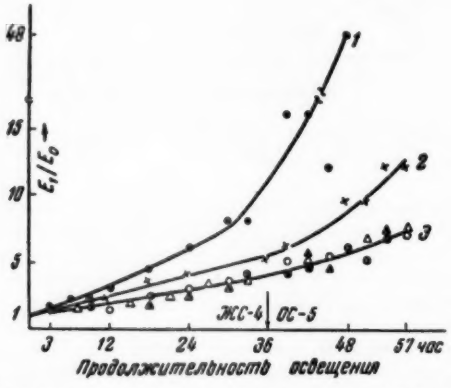

FIG. 4.—Kinetics of structure formation in SKB during irradiation through ZhS-4 and OS-5 light filters. Sulfur concentration: *1*—0%; *2*—0.25%; *3*—0.5%; *4*—2.5%.

concentration, is the same as under the action of antioxidants which are photosensitizers[11]. Evidently the reason for the retardation of the process is the same in both cases and is explained by the light-filtering action of these materials.

This is indicated by the following:

1. The combination of sulfur with butyl rubber is slower when the rubber contains 2.5% of sulfur than with 0.5% (Figure 3).
2. Because of the light-filtering action of the sulfur, the relative magnitude of the process of degradation increases with an increase in sulfur concentration, whereas the modulus value here goes through a maximum peak at the optimum.
3. When SKB with sulfur is irradiated through the light filter ZhS-4 (transmitting light with $\lambda > 380$ mμ), only its light-filtering action is exhibited (Figure 4).

Thus sulfur either reinforces structure formation in SKB (light through UFS-1) or weakens it (through ZhS-4), depending on the composition of the light, whereas when SKB + 1.5% S is irradiated through light filter BS-8 (transmitting light with $\lambda > 350$ mμ), the light-filtering and structure-forming effects of sulfur compensate for one another, and its presence has no effect on the light-aging of SKB.

It has been shown through this work that the optimum peak of photovulcanization in butyl rubber is explainable by an increasing dominance of the degradation processes involving the scission of the sulfur structures formed, as the irradiation is prolonged. The breakdown of these structures may be observed also during the photovulcanization of SKB. The retardation of this process with an increase in the sulfur concentration above 0.5–1% is explained by its light-filtering action.

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THE NATURE OF OPTIMUM VULCANIZATION IN NATURAL RUBBER *

A. S. Kuzminskiĭ and V. F. Chertkova

Scientific Research Institute of the Rubber Industry, USSR

The vulcanization of natural rubber is accompanied by a considerable change in mechanical properties as the vulcanizate is formed. With sulfur as the vulcanizing agent an optimum is observed in the change in tensile strength and other physical properties. In many studies[1] the presence of an optimum vulcanization has been considered as the result of the superimposition of two processes: (1) the structure-forming action of sulfur and (2) the degrading action of the oxygen, which causes a reversion of vulcanizates. We have established[2] that the oxidative degradation of natural rubber in the vulcanization process proceeds extremely slowly and cannot have any substantial effect on the tensile strength of vulcanizates. To resolve the question as to the true causes of the reversion of vulcanizates in "overvulcanization", several series of experiments were set up.

In the first series the mobility of sulfur bonds was studied in natural rubber vulcanizates containing various accelerators[3] by the use of the sulfur radioisotope[4] S^{35} with a method described earlier[5].

The results of these experiments shown in Figure 1 indicate the "concentration" of mobile links in the vulcanizate to change proportionately with the change in tensile strength and the maximum density of mobile polysulfide links thus corresponds to optimum vulcanization according to tensile strength. The modulus likewise changes during the course of vulcanization, proportionately to the density of the intermolecular crosslinks formed.

The formation of a complex three-dimensional network proceeds continually through all the various stages of the process up to the optimum. The increase in network density in the vulcanizates being formed, up to the optimum, is accompanied by a steady substantial rise in tensile strength. Further vulcanization, however, causes a decrease in network density and a drop in tensile strength.

In a second series of experiments with vulcanizates at various stages of the process the polysulfide bonds were removed by extraction with sodium sulfite. When this occurred a decrease in the tensile strength of the vulcanizates was observed, which was especially marked at optimum vulcanization (Figure 2, Curve *2*).

In a third series of experiments, vulcanization was achieved with tetramethylthiuram disulfide (TMTD) without added sulfur. It is known that TMTD forms monosulfide bonds in rubber which are stable under the usual vulcanization conditions (a temperature of 143° C). Figure 2 (Curve *3*) shows that no reversion is observed in vulcanization with TMTD.

The results of the three series of experiments given show definitely that the

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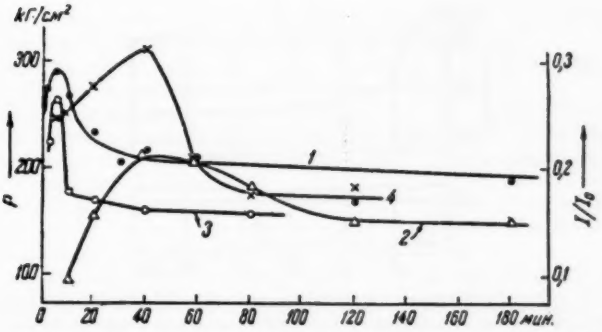

FIG. 1.—Kinetics of the change in tensile strength and relative mobility of sulfur links in the process of natural rubber vulcanization. *1*—Tensile strength *P* of thiuram vulcanizate; *2*—tensile strength of diphenylguanidine vulcanizate; *3*—relative mobility of sulfur links in thiuram vulcanizate; *4*—relative mobility of sulfur links in diphenylguanidine vulcanizate. The abscissa represents time in minutes, the left ordinate tensile strength in kg/cm², the right ordinate the relative activity.

presence of mobile polysulfide bonds in vulcanizates is a necessary condition for their reversion.

It is evident that two concurrent tendencies are exhibited in all the stages of the vulcanization process: the formation of new sulfur bonds and the decomposition of existing ones. During the various stages of vulcanization, as long as there is a sufficient amount of free sulfur in the system, the formation of sulfur bonds is the predominating process. The disappearance of free sulfur markedly lowers the rate of formation of new bonds, and hence the decomposition of the structures already formed becomes the predominating process. The point where the rates of formation and decomposition of mobile sulfur bonds become equal corresponds to optimum vulcanization.

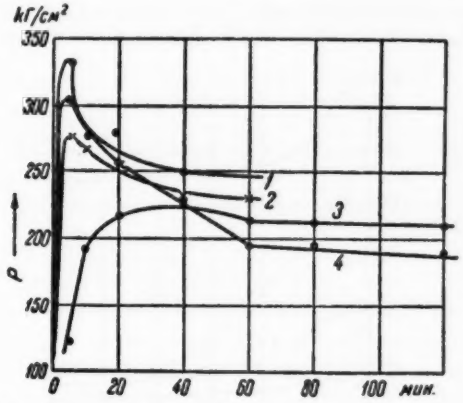

FIG. 2.—Kinetics of the change in tensile strength in vulcanizates, after the removal of the free ingredients and the polysulfide links, at various stages of vulcanization: *1*—tensile strength *P* of the original vulcanizates; *2*—tensile strength of vulcanizates after the removal of their polysulfide links by extraction with Na_2SO_3; *3*—tensile strength of vulcanizates obtained with thiuram and no sulfur; *4*—tensile strength of vulcanizate after extraction with acetone. The abscissa represents vulcanization time in minutes, the ordinate the tensile strength *P* in kg/cm².

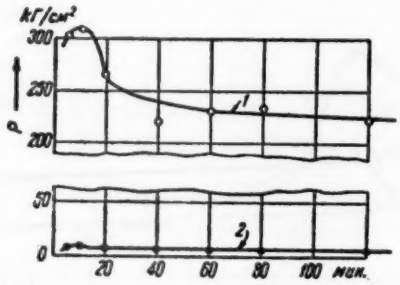

FIG. 3.—Kinetics of the change in tensile strength of vulcanizates after swelling to the limit in vaseline oil, at various stages of vulcanization. *1*—Tensile strength *P* before swelling; *2*—tensile strength after the swelling of the vulcanizates. The abscissa represents vulcanization time in minutes, the ordinate tensile strength *P* in kg/cm².

Naturally our outline of the situation is oversimplified, expressing only the main features which characterize the vulcanization process without including many of its details.

The optimum is exhibited especially clearly in the vulcanization of crystallizing rubbers (natural and butyl rubbers). Raw plasticized natural rubber is characterized by a very low tensile strength (3–4 kg/cm²). When vulcanized to the optimum, its tensile strength increases approximately 100 fold.

The high tensile strength of natural rubber vulcanizates gives evidence of its crystallization at high elongation deformations. In the deformation of raw rubber a flow takes place which prevents crystallization. Even a slight development of the three-dimensional network, however, is sufficient to prevent flow in the polymer and to maintain the structure unchanged until the onset of crystallization[6]. Consequently a high tensile strength may be achieved in natural rubber vulcanizates only after the incipient formation of the three-dimensional structure.

The question arises, is the change in the tensile strength of vulcanizates at the various stages of the process directly related to the change in the density

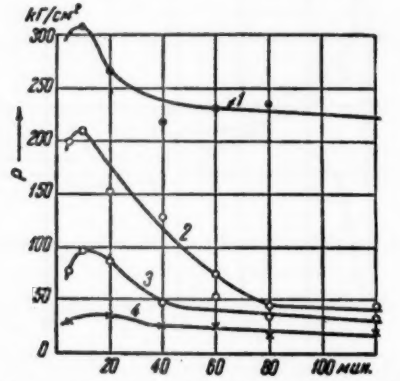

FIG. 4.—Effect of test temperature on the kinetics of the change in tensile strength of vulcanizates in the vulcanization process: *1*—at 25° C; *2*—at 70°; *3*—at 100°; *4*—at 140°. The abscissa represents vulcanization time in minutes, the ordinate tensile strength *P* in kg/cm².

and energy of the crosslinks, or to their favorable influence on conditions of orientation, and finally of crystallization, in the vulcanizate?

To clarify the direct causes underlying the change in tensile strength during vulcanization, special experiments were set up.

In the first set of experiments, vulcanizates at various stages of the vulcanization process were swelled to the limit in vaseline oil[7]. Then the tensile strength of the swelled vulcanizates was measured. The results of the experiments are presented in Figure 3.

In another series of experiments the tensile strength of vulcanizates at different stages of vulcanization was measured at temperatures of 25–140° C. The results are given in Figure 4.

It is known that the tensile strength of a material depends on the number and strength of the chemical bonds found in the cross section of the break, as well as on the strength of the intermolecular interactions which are overcome in the break. The swelling of vulcanizates, as well as a rise in their testing temperature, causes a sharp drop in the intermolecular interactions, and consequently makes it possible to evaluate the effect of the latter on the tensile strength of vulcanizates.

As Figures 3 and 4 show, swelling and an increase in the testing temperature of vulcanizates cause a sharp decrease in their tensile strength. Thus, for example, the tensile strength of a swelled vulcanizate differs little from the tensile strength of raw rubber. Consequently the role played by crosslinks consists mainly in their favorable influence on the orientation and crystallization of molecular chains. By creating artificial conditions favoring crystallization, we do not make it possible for sulfur crosslinks to exhibit this influence. The crosslink junctions whose concentrations (density) are low in approaching the crosslink concentration in raw rubber, are evidently the nuclei of crystallization.

It is known[8] that an increase in the amount of sulfur combined in the process of rubber vulcanization causes a progressive increase in the crystalline phase up to optimum vulcanization. The results given agree fully with the conclusions drawn above as to the decisive influence of the bonds formed during vulcanization on the conditions of crystallization and the tensile strength of vulcanizates.

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VULCANIZATION OF ELASTOMERS. 21. VULCANIZATION OF NATURAL RUBBER WITH THIURAM DISULFIDES. VI *

WALTER SCHEELE AND KLAUS HUMMEL

KAUTSCHUKINSTITUT, TECHNISCHE HOCHSCHULE, HANNOVER, GERMANY

INTRODUCTION

By extensive research, we have been able to clarify several reactions which take place in the vulcanization of natural rubber and two synthetics (Buna and Perbunan) with thiuram compounds in the presence of zinc oxide[1,2]. The first order transformation of thiuram disulfide to a temperature-independent, final value of zinc dithiocarbamate goes more slowly than the reduction of the concentration of the thiuram disulfide, which also follows a first order law. This is true in both "pure" and "accelerated" thiuram vulcanization. We speak of "pure" thiuram vulcanization when the crosslinking of the rubber is done with thiuram disulfide or with thiuram monosulfide plus sulfur (1 mole monosulfide per gram atom of sulfur) and of "accelerated" thiuram vulcanization when thiuram di- or monosulfides plus x or $(x + 1)$ gram atoms of sulfur are used. Zinc oxide is present in every case[1].

From the just mentioned difference in rates, it was concluded that vulcanization occurs through the formation of an intermediate compound, and after thorough study of the dependence of the rate of thiuram disappearance and of dithiocarbamate formation on the concentration of zinc oxide in the rubber compound, it was concluded that the intermediate compound forms in contact with zinc oxide. Actually, the crosslinking reaction, whose kinetics are readily followed by measurement of the reciprocal equilibrium swelling, and which is also found to follow a first order course, comes much nearer to having the same rate as the dithiocarbamate formation, than it does to having that of the thiuram disappearance.

The question which needs further clarification has to do with the kinetics of sulfur combination, i.e., sulfur which is not extractable by organic solvents, which remains in the rubber, and which is either bound in the crosslinking sites as "bridge-sulfur", or by the molecular chains in the form of fragments of thiuram disulfide, or that occurring in the vulcanizate as insoluble sulfur compounds. It should be noted here that we could find neither zinc sulfide nor sulfate formation in thiuram vulcanizates. We wish to contribute to the answer to this question with the quantitative data of this article for the case of "pure" thiuram vulcanization.

EXPERIMENTAL RESULTS AND DISCUSSION

The work was carried out with pale crepe, which had been thoroughly extracted with acetone in a Soxhlet apparatus. The vulcanizates which were

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by W. D. Wolfe, from *Kautschuk und Gummi*, Vol. 11, WT 267-272, October 1958. To save space, a table of data has been omitted.

prepared at different temperatures and with various reaction times, were, as usual, extracted at room temperature and in the dark, with ethyl acetate, freed of solvent by heating for 12 hours in an oven at 60° C, and then analyzed for their sulfur content. The method worked out by Bauminger[3] was used in principle for this analysis, although it was somewhat modified. We will report more fully on this at a later time. We determined the thiuram and dithiocarbamate content of the extracts and in several cases we also studied the kinetics of the crosslinking by measurements of the swelling of the vulcanizates in benzene.

All the studies were made with rubber compounds which contained 84.1 g natural rubber, 10 g zinc oxide, and 5.93 g tetraethylthiuram disulfide (TETD) in 100 g of compound. We convinced ourselves, by elementary analysis of the unvulcanized mixture and the unextracted vulcanizates for each series of experiments that no volatile sulfur compounds escaped during vulcanization. The sulfur content of the raw compound agreed with that of the unextracted vulcanizate.

The experimental results show that the sum of the TETD, ZnDEDC, and bound S, as per cent based on the original amount of thiuram disulfide is in no case equal to 100%, so the difference between 100 and the above sum in each case must represent the portion of sulfur in the extract which occurs in a compound which is neither thiuram disulfide nor dithiocarbamate. The data on the 110° C samples show especially clearly how these portions go through a maximum in the intermediate reaction times. The following example will show the way in which the sulfur content of the vulcanizates is calculated. 1.00 g of vulcanizate was extracted and then dried. The residue weighed 0.926 g = 92.6% of the sample. Elementary analysis of 185.8 mg of this residue showed 1.365 mg of sulfur. Now in accordance with the S content of TETD (43.25% S), the original mixture contained 2.564% S. Hence the sulfur content of the vulcanizate is

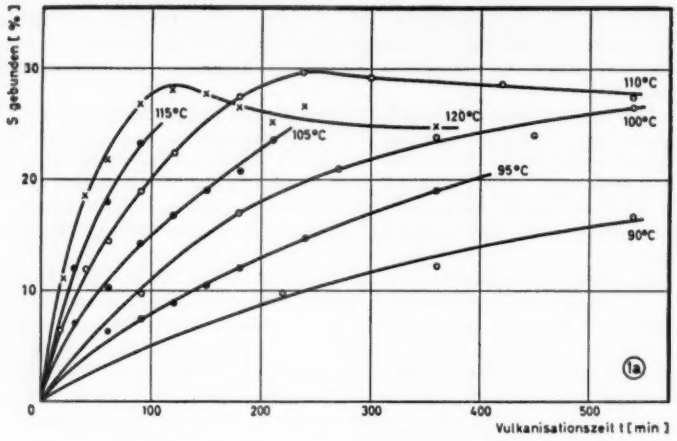
$$\frac{(1.365)(92.6)}{(185.8)(2.564)} = 26.5\%$$

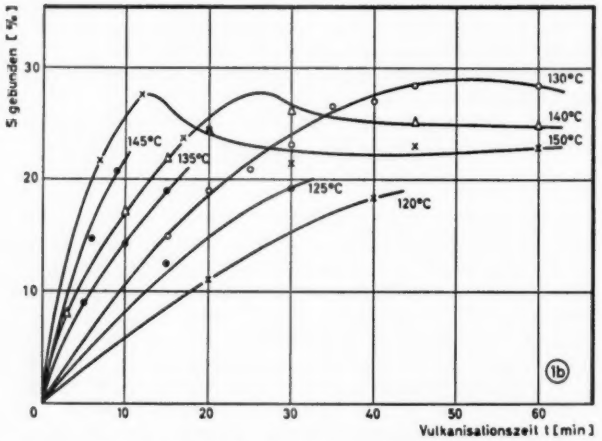
Thus x% S corresponds to x mole % TETD.

In Figures 1a and 1b, we show the change in bound sulfur with vulcanization time for temperatures 90°–120° and 120°–150° C, respectively. In all cases the amount rises on a curve bending away from the ordinate, goes through a poorly defined maximum and then approaches a limiting value. The maximum does not show clearly and would no doubt change with variations in the composition of rubber compound because of the dependence of the rate of thiuram disappearance and dithiocarbamate formation on the zinc oxide content. In the present case, the high value of 30% and the low of 27% for the maximum are read from the course of the curves. These highest and lowest values do not follow a temperature pattern. After all, we find a pattern for the combination of sulfur which corresponds in all respects to the results obtained by Hauser and Brown[4], so that we confirm their data in a qualitative way.

Now it has been repeatedly and clearly shown by us, that in cases of vulcanization with tetraalkylthiuram disulfides, (zinc oxide always present) the limiting conversion to zinc dithiocarbamate is under all circumstances independent of the temperature and amounts to two thirds (66.6 mole %) of the original thiuram disulfide; and if nothing else forms but zinc dithiocarbamate,

then 33.3 mole % of the thiuram disulfide should be involved directly in cross-linking, that is, the completely reacted vulcanizates should contain 33.3% of the sulfur of the original thiuram disulfide. The limiting value which the bound sulfur in the vulcanizates approaches is shown by plotting the sulfur



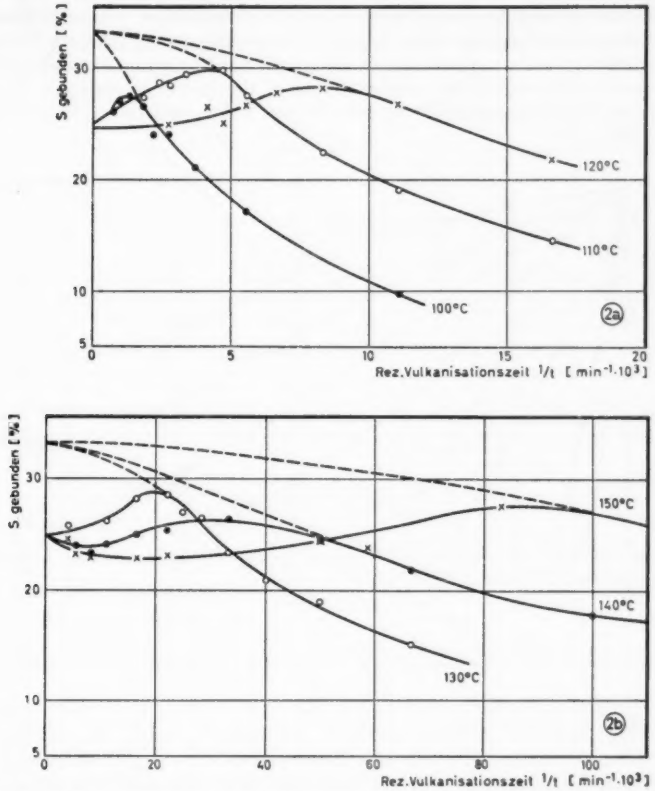


FIGS. 1a and 1b.—Change with time of the bound sulfur in the vulcanization of natural rubber with tetraethylthiuram disulfide. Ordinate: Bound sulfur. Abscissa: Vulcanization time, t min.

content values against the reciprocal of the vulcanization time and then extrapolating the curves to $1/t = 0$. This is shown in Figures 2a and 2b. Because of the maxima which show in Figures 1a and 1b, this extrapolation cannot be done accurately. The course of the curve for each temperature however shows (in the broken lines) that a limiting value of about 25% is approached practically independent of the temperature. Thus the sulfur content of the fully

reacted vulcanizates is shown to be lower than expected; and it must therefore follow that about 8% of the sulfur must be undetermined in the extracts. Indeed even the use of the spectrophotometric method could not reveal in what compound the sulfur existed.

It should be noted that the sum of the limiting value of dithiocarbamate formed (66.6 mole %) plus the sulfur increase (25%), both based on the original



FIGS. 2a and 2b.—Demonstration of the determination of the limiting value for bound sulfur in the vulcanization of natural rubber with tetraethylthiuram disulfide. Ordinate: Bound sulfur. Abscissa: Reciprocal vulc. time $1/t(\text{min}^{-1} \cdot 10^3)$.

thiuram disulfide, amounts to 91.6%. Thus, it is practically the same as the limiting value of dithiocarbamate formed in the reaction of thiuram disulfide with zinc oxide in absence of rubber[5].

The limiting value for the bound sulfur which we find is quantitatively in agreement with analogous figures by Hauser and Brown[4]. In the meantime, independently, this same value was found by Dogadkin[6], so there can be no doubt of the fact that 25% of the sulfur based on the original thiuram disulfide, remains bound in the vulcanizate in pure thiuram vulcanization.

The occurrence of the maxima in Figures 1a and 1b leads us to look for the law for the rise of sulfur content in the region along the curves before the maxima are reached. The curves of Figure 3 are obtained by plotting the logarithms of the values of the analytical results against the reciprocals of vulcanization times. (See also the broken lines in the curves of Figures 2a and 2b.) It can be seen that they converge as $1/t$ falls and can be brought to a point on the ordinate axis; and because—as has often been pointed out by us—the dithiocarbamate content, in cases of pure thiuram vulcanization, reaches a temperature independent limiting value (a fact which greatly strengthens the assurance of the existence of a temperature independent limiting value for bound sulfur) we should conclude, on the good evidence of the curves of Figure 3, that the bound sulfur would approach a constant end value, and this value should be about 33%.

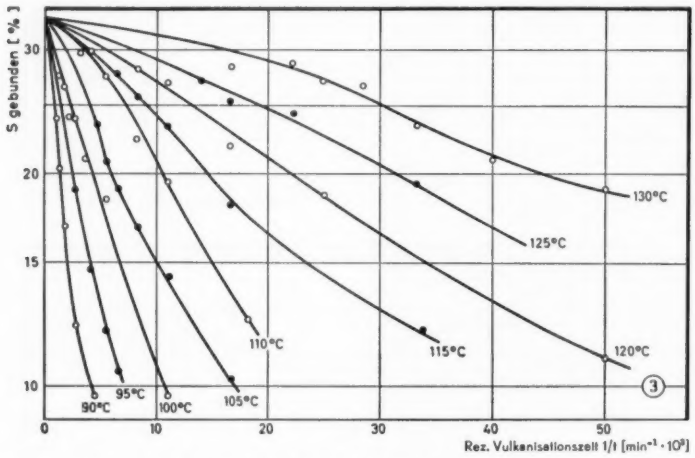
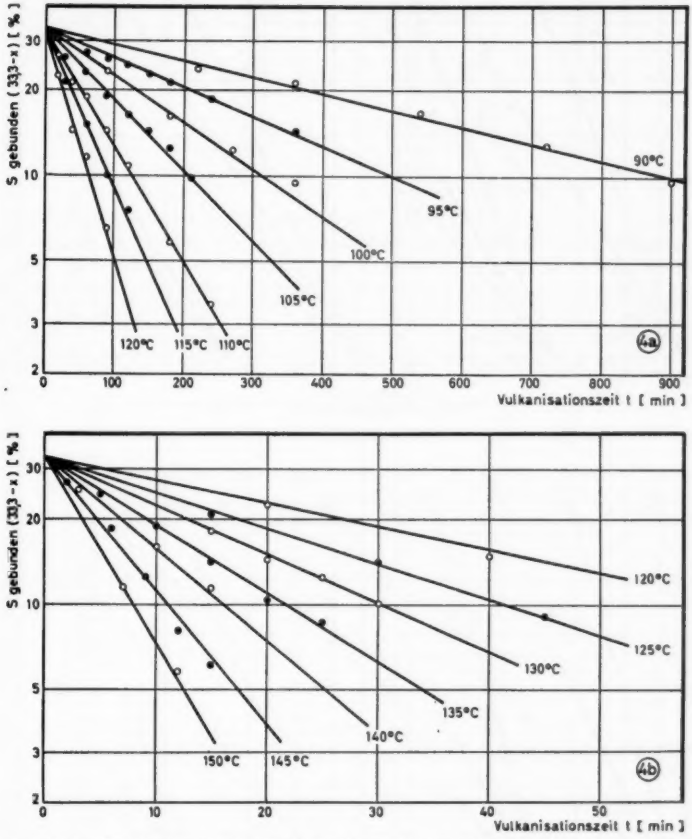


FIG. 3.—Demonstration of the limiting value for bound sulfur as indicated by the rising sections of the curves in Figures 1a and 1b. Ordinate: Bound sulfur. Abscissa: Reciprocal of vulc. time $1/t(\text{min}^{-1} \cdot 10^3)$.

If we take the difference $(33.3 - x)$, between the limiting value and the conversion (x), and then plot the logarithms of these values against the vulcanization times, we obtain the curves of Figures 4a and 4b. These curves show that the rate of change in the bound sulfur of the vulcanizates follows a first order law for about as long as its amount in the vulcanizate is increasing. As long as the bound sulfur is increasing, the same relations, from a kinetic viewpoint, hold as for thiuram disappearance and for dithiocarbamate formation, which satisfy the first order law in by far the greater portion of the reaction period.

Now we should think that there should be a kinetic relation between the increase in bound sulfur and crosslinking such as seems to be the general rule for other vulcanization reactions[7]. Hence, we should expect to find that the increase of bound sulfur up to the maxima shown in Figures 1a and 1b, goes at the same rate as the formation of dithiocarbamate; for, as has been previously demonstrated, the first order crosslinking (shown by rate of change in the reciprocal equilibrium swelling) proceeds at the same rate as the formation of

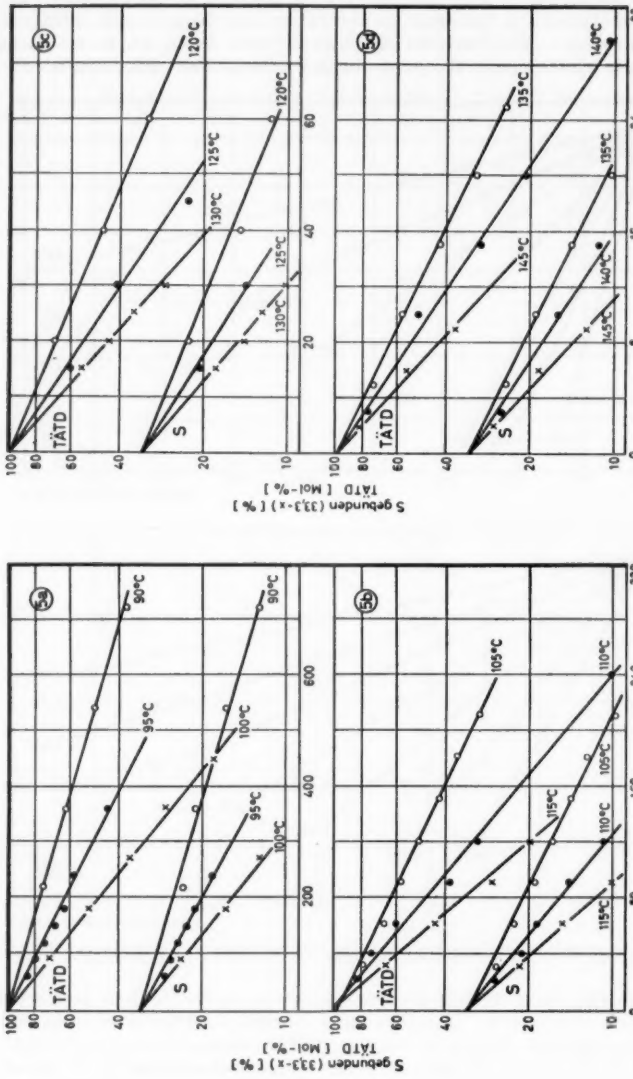
dithiocarbamate. However, closer inspection shows that this is not the case; it is quite surprising to find that the rate of increase in bound sulfur, up to about its maximum, is the same as the rate of decrease in concentration of thiuram disulfide. We illustrate this with Figures 5a to 5d, in which both reactions are plotted from the experimental data as first order reactions. It



FIGS. 4a and 4b.—Combination of sulfur in a first order reaction, as indicated by the rising sections of the curves in Figures 1a and 1b. Ordinate: Bound sulfur. Abscissa: Vulcanization time t (min).

can be seen that the curves at the same temperature for thiuram decrease and bound sulfur run parallel. Hence we must conclude that the rates are the same.

Even though the identity in rates of TETD decrease and of ZnDMDC increase which has been met with, is, in our opinion, no accident, yet it needs to be shown if this also holds for other molar ratios of TETD and ZnO. That sulfur is bound by the rubber faster than dithiocarbamate is formed with the accompanying "bridge forming" seems to be assured (see also Hauser and Brown[4]).



FIGS. 5a to 5d.—Demonstration of identity of rates for thiuram decrease, and bound sulfur increase in the vulcanization of natural rubber with tetraethylthiuram disulfide. Ordinate: Bound sulfur (33.3-x) % and TETD (mole %). Abcissa: Vulcanization time t (min).

TABLE I

RATE CONSTANTS FOR THIURAM DECREASE (k_{TETD}), INCREASE IN BOUND SULFUR (k_S), AND DITHIOCARBAMATE FORMATION (k_{DC})

Temp. ° C	$k_{TETD} \cdot 10^3$	$k_S \cdot 10^3$	$k_{DC} \cdot 10^3$
95	2.36	2.40	1.00
100	3.84	3.86	1.71
105	5.78	5.78	2.65
110	9.44	9.36	3.70
115	12.8	12.8	5.55
120	18.6	18.3	7.86
125	30.3	28.8	12.8
130	40.4	39.8	18.2
135	54.8	56.0	24.1
140	76.8	75.5	31.3
145	108.5	109.	51.9

The fact, very important, it seems to us, that at least in the first stages of vulcanization, the sulfur is bound by the rubber at the same rate as the thiuram disulfide concentration decreases, is also shown in Table I, in which are tabulated, the first order rate constants calculated from the experimental data, (k_{TETD}) for thiuram decrease, (k_S) for bound sulfur, and (k_{DC}) for dithiocarbamate formation. We have refrained from presenting the kinetics of the dithiocarbamate formation graphically but wish to emphasize that the values

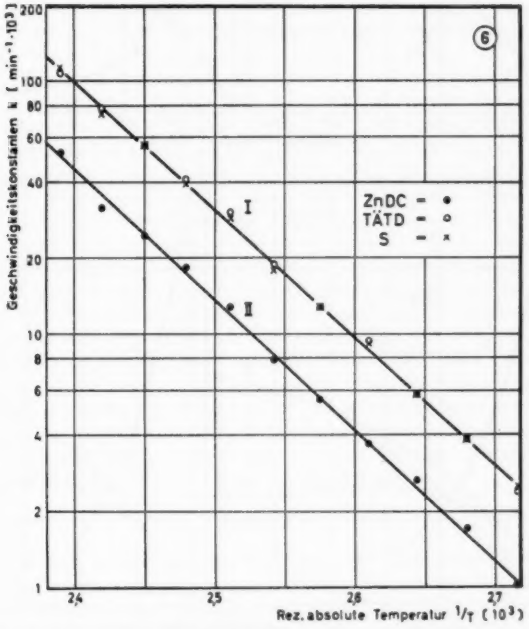
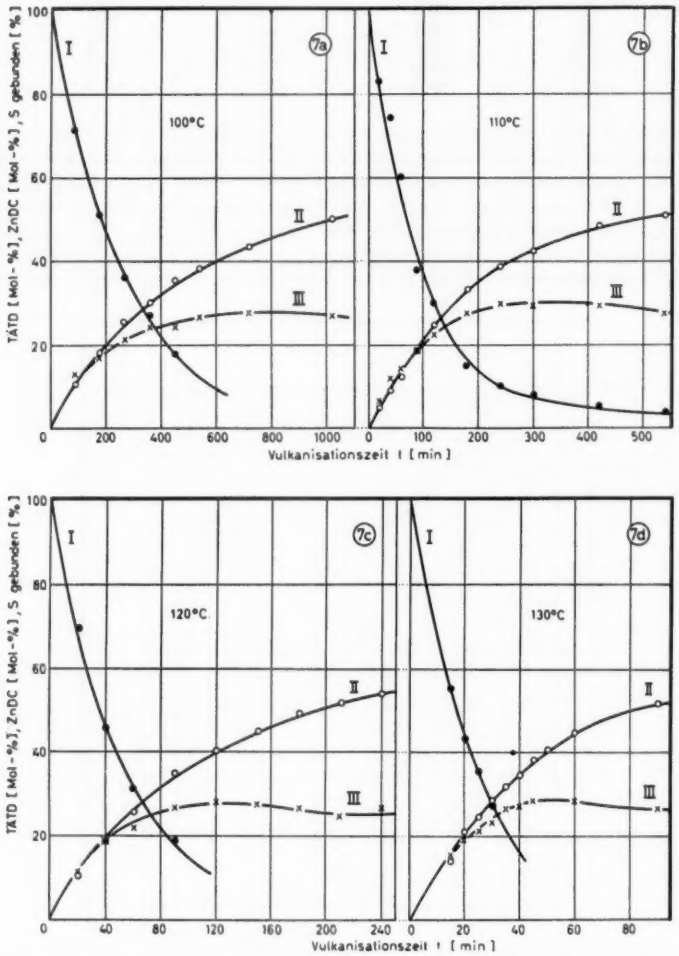


FIG. 6.—Temperature dependence of the first order rate constants for thiuram decrease and bound sulfur increase (I) as well as for dithiocarbamate formation (II). Ordinate: Rate constants k ($min^{-1} \cdot 10^3$). Abscissa: Reciprocal absolute temperatures ($1/T$) (10^3).

are in complete agreement with results which have been repeatedly reported. When the logarithms of these rate constants are plotted against the reciprocal of the absolute temperature, we get the curves of Figure 6. It is seen that the constants k_{TETD} and k_S fall on the same curve (I) while the values for k_{DC} are considerably lower at the same temperatures and fall on (II). There can be no doubt that sulfur in a thiuram vulcanization becomes bound without simultaneous formation of "bridges", quite a surprising result.

The curves of Figure 6 are practically parallel which shows that all these



FIGS. 7a to 7d.—Thiuram decrease (I), dithiocarbamate formation (II) and increase in bound sulfur (III) in the vulcanization of natural rubber with tetraethylthiuram disulfide.

reactions in a thiuram vulcanization have about the same activation energy. A value of 23 kcal/mole was calculated for them. Hence we should conclude that the maxima in Figures 1a and 1b are the same.

It is evident from the above and from previously reported researches that a complex process takes place in the reaction of thiuram disulfides with rubber in the presence of zinc oxide. To help clarify the three features of this thiuram vulcanization which have been closely studied, we have presented in Figures 7a to 7d, the decrease in thiuram disulfide concentration, I, the dithiocarbamate formation, II, and the bound sulfur, III, plotted against the time of vulcanization for the temperatures 100°, 110°, 120° and 130° C. It should be mentioned that corresponding graphs for other temperatures give similar information. Curves I and II, I and III, as well as II and III all intersect at about the same value and this is true for other temperatures. This would be expected in light of the slight variations in the almost identical activation energies shown above for the decrease in thiuram and the formation of dithiocarbamate. We can convince ourselves from the data that the bound sulfur in the vulcanizate is regularly equal to one third of the consumed thiuram disulfide. At the point of intersection of Curves I and II, this value is 25% = 75/3. At this stage of the vulcanization, the product has no technically valuable physical properties. As the process continues, the formation of dithiocarbamate and with it the crosslinking, increase considerably, yet the rubber does not bind additional sulfur. Nevertheless, the vulcanizates take on their technically valuable physical properties first at this time. Thus we can deduce the fact that the sulfur content of a thiuram vulcanizate is no criterion of the state of vulcanization.

However interesting and important are the foregoing relations for the combining of the sulfur and likewise the relations previously revealed for the thiuram vulcanization of synthetic rubbers in the discussion of the nature of the vulcanization process yet after thoughtful consideration on our part and review of all the relationships which we have disclosed, they do not permit us to draw firm conclusions which would make other research projects unnecessary, and which could yield the foundations for formulation of a reaction mechanism which includes all of the quantitative observations. To be sure, we have earlier proposed a chemism for discussion which makes plausible the two-thirds transformation of thiuram disulfide to dithiocarbamate and which leads to the acceptance of a hypothesis of disulfide bridge formation[8]. Yet the information given in this paper still allows the idea of the formation of C—C bridges to come up anew. In spite of securing much important supplementary knowledge, the present research has pointed to the fact that quantitative data on bound sulfur in a thiuram vulcanization is a rather unspecific criterion, and it is evident that the dependence of the sulfur content of the vulcanizate on the reaction time is without doubt the result of the interaction of several things, and as we see it, a correct explanation is impossible without further study.

SUMMARY

Bound sulfur in a pure thiuram vulcanizate increases relatively rapidly at first at all temperatures, reaches a poorly defined maximum at about 27 to 30%, independent of temperature, and then recedes slightly to reach a limiting value of 25% also independent of temperature, based on the original thiuram disulfide.

The rise in sulfur content at the start points to a temperature-independent

limiting value of 33%. It is shown that the combination of sulfur in this region initially follows a first order reaction, and goes at the same rate as the reduction in concentration of thiuram disulfide.

It can be seen from the above that sulfur may be combined in thiuram vulcanization without simultaneous crosslinking.

The dithiocarbamate formation increases rapidly in the region of longer vulcanization times, after the maximum in bound sulfur has been reached, without further combination of sulfur with the vulcanizate.

The rate constants for thiuram decrease, for dithiocarbamate increase and for sulfur combination were calculated. The temperature dependence of each of these reactions has practically the same activation energy, 23 kcal/mole.

The bound sulfur content of the vulcanizates in pure thiuram vulcanizations is no criterion of the state of vulcanization.

ACKNOWLEDGMENTS

The authors thank the Continental Gummi-Werke A.G., Hannover, for the gift of natural rubber. The Chemische Werke Hüls A.G., Marl, as well as Farbenfabriken Bayer, A.G., Leverkusen, aided us by providing solvents and chemicals. We wish to thank them sincerely.

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[7] In vulcanization with sulfur in the presence of zinc benzothiazolyl mercaptide, the reduction in concentration of sulfur and the crosslinking are both reactions of the first order and of the same rate; the two reactions are not at the same rate when zinc stearate is present [see Lorenz, O. and Echte, E., *Kautschuk u. Gummi* **10**, WT 23 and WT 81 (1957); the same authors, *Verhandlungsber. d. Kolloid-Ges.* **18**, 142 (1958)]. Also in vulcanization with sulfur accelerated by zinc dithiocarbamate, the reduction in concentration of free (unbound) sulfur corresponds to the crosslinking [Scheele, W. and Birghan, Kl., *Kautschuk u. Gummi* **10**, WT 214 (1957)].

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THE REACTIONS OF AMINES AND SULFUR WITH OLEFINS. IV. THE CHEMICAL AND THERMAL DECOMPOSITIONS OF N,N′-THIOBISAMINES AND THEIR REACTIONS WITH OLEFINS *

R. W. SAVILLE

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, WELWYN GARDEN CITY, HERTS., ENGLAND

Parts I–III of this series[1] described the use of combinations of secondary amine and sulfur and of N,N′-thiobisdiethylamine $Et_2N \cdot S \cdot NEt_2$ as olefinic sulfurating agents. The introduction[1] of N,N′-thiobisamines, $(RR'N)_2S_x$, as vulcanizing agents for rubber justifies a more detailed study of their properties.

Chemical decomposition of N,N′-thiobisamines.—The reactivity of the N—S bond in sulfenamides, $RR'N \cdot SR''$, with electrophilic reagents has been studied by several workers, but little attention has been paid to the comparable reactivity of N,N′-thiobisamines. Blake[3] showed that carbon disulfide and carbon oxysulfide caused N—S bond fission in the thiobisamines and led to thiuram sulfides, $(R_2N \cdot CS)_2S_x$, and thiocarbamoyl derivatives, respectively:

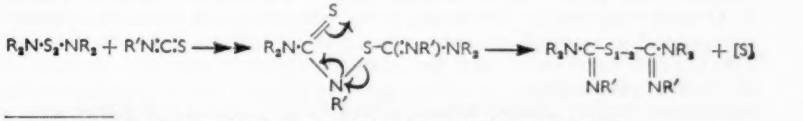
$$R_2N \cdot S_x \cdot NR_2 + 2CSX \longrightarrow R_2N \cdot C(:X) \cdot S_{x+2} \cdot C(:X) \cdot NR_2$$

In dilute hydrochloric acid the thiobisamines liberate amine, presumably in the manner: $R_2N \cdot S_x \cdot NR_2 + 2HCl \longrightarrow 2R_2NH + S_xCl_2$, the sulfur halide then yielding sulfur, sulfur dioxide, and hydrogen sulfide[4]. Indicative of preferential N—S, rather than S—S, bond fission in dithiobisamines, $R_2N \cdot S_2 \cdot NR_2$, is Lecher and Weigel's observation[5], now confirmed, that sulfurous acid affords substances formulated as $[R_2NH^+]_2[S_2O_3H^-]_2$. Treatment in a solvent with hydrogen sulfide rapidly affords sulfur and the parent amine. Similar rapid fission of the N—S bond is observed in the reaction with thiols at room temperature, in the solid state or in ethanol solution, the amine and the tetrasulfide derivative from the thiol being formed in high yield:

$$(C_4H_8ON)_2S_2 + 2C_6H_4Me \cdot SH \longrightarrow 2C_4H_9ON + C_6H_4Me \cdot S_4 \cdot C_6H_4Me$$
$$(C_4H_9ON = \text{morpholine.})$$

This constitutes a new preparative method for organic tetrasulfides. Thiolacids with thiobisamines, and thiols with sulfenamides, react similarly, and this is responsible for the catalytic action of thiols on rubber vulcanization by accelerators containing N—S bonds.

Blake's work[3] has now been extended to *iso*thiocyanates: methyl and benzyl *iso*thiocyanate react readily with dithiobisamines:[6]



* Reprinted from the *Journal of the Chemical Society*, August, 1958, pages 2880–2888.

The effect of Friedel-Crafts catalysts on the N—S bond in thiobisamines has not been examined in detail, but Burg and Woodrow[7] found that boron trifluoride forms stable complexes, presumably by utilization of the unshared electrons of the nitrogen. The reduction of N,N-dithiobismorpholine with lithium aluminum hydride gives morpholine, hydrogen sulfide, and sulfur.

Thermal decomposition of N,N′-thiobisamines.—N,N,′-Dithiobisdibenzylamine at 140° *in vacuo* gives dibenzylammonium hydrogen sulfide and N-benzyl-(thiobenzamide), which are also formed by reaction of dibenzylamine with sulfur at 140° (cf. Moore and Saville[1]):

$$Ph\cdot CH_2\cdot NH\cdot CH_2\cdot Ph + 2S \longrightarrow H_2S + Ph\cdot CH_2\cdot NH\cdot CS\cdot Ph$$

Hydrogen sulfide and amine are also formed when N,N′-dithiobis-(2-ethylaminopropionitrile) is heated at 140°, but in this case, and in the reaction of 2-ethylaminopropionitrile with sulfur at 140°, the expected thioamide could not be identified.

Thermal reaction of N,N′-thiobisamines with olefins.—Negligible reaction occurs between N,N′-mono- or -di-thiobismorpholine and cyclohexene or 2,6-dimethylocta-2,6-diene at 140°, in contrast to the extensive reaction[1] of cyclohexene with N,N′-monothiobisdiethylamine at 140°.

With cyclohexene at 140° N,N′-dithiobisdibenzylamine yields a complex mixture: (*a*) benzyl cyclohexyl sulfide and mixed sulfides R_2S_x (R = $Ph\cdot CH_2$, C_6H_{11}, C_6H_9; x = 1–2); (*b*) polymeric sulfides of the type $Ph\cdot CH_2\cdot S_x\cdot C_6H_{10}S_x\cdot CH_2\cdot Ph$; (*c*) N-benzylthiobenzamide; (*d*) dibenzylamine; (*e*) N,N′-trithiobisdibenzylamine; and (*f*) traces of benzylamine, benzaldehyde, and toluene. Considerable migration of benzyl groups occurs during the above reaction, as in reactions of other benzyl-substituted sulfur compounds, e.g., benzyl alkyl xanthates and benzylsulfonium compounds[8], and (benzylthio)benzothiazole[9], and the smooth isomerization of sulfidimines[8] fails with the dibenzyl compound, $(Ph\cdot CH_2)_2S\cdot N\cdot SO_2\cdot Ar$. The monosulfide in fraction (*a*) was identified as its sulfone and by infrared spectroscopy, and the polysulfides in (*b*) by spectroscopy and by reduction with lithium aluminum hydride to toluene-ω-thiol in high yield, together with a polymeric monosulfide analogue and a cyclohexanedithiol, of unknown composition, isolated as its bis-2,4-dinitrophenyl sulfide (minor amounts of cyclohexane- and cyclohex-2-ene-thiol were also isolated).

The formation of benzaldehyde, benzylamine, and toluene in the above reactions of N,N′-dithiobisdibenzylamine is attributed to Willgerodt reactions of the type examined by King and McMillan,[10] and thioamide alkylation:[1]

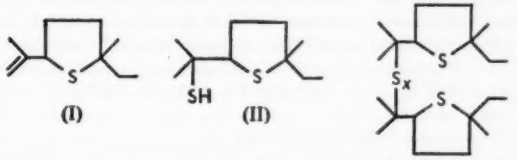
$$Ph\cdot CS\cdot NH\cdot CH_2\cdot Ph + (Ph\cdot CH_2)_2NH \longrightarrow Ph\cdot CH_2\cdot NH_2 + Ph\cdot CS\cdot N(CH_2\cdot Ph)_2$$

followed by hydrogenolysis of benzyl groups of the amine[11].

With 1-methylcyclohexene at 140° N,N′-dithiobisdibenzylamine gives the thioamide and a high yield of dibenzylamine. The main product had a lower H:C ratio than that of the parent olefin, suggesting the presence of benzyl groups, and its infrared spectrum was consistent with the presence of benzyl 1-methylcyclohexyl sulfide and di-(1-methylcyclohexyl) sulfides. Presence of the former was confirmed by oxidation to the sulfone. Hydrogenolysis of the sulfuration product yielded toluene-ω-thiol in large amount, together with a small proportion of 1-methylcyclohexanethiol and di-(1-methylcyclohexyl)

monosulfide; from the spectral data 2-methylcyclohexanethiol may also have been present, and the mechanistic significance of this is discussed below.

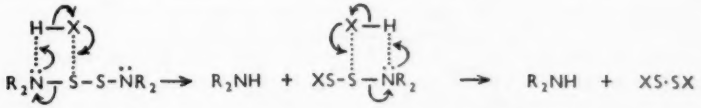
Olefinic sulfuration with N,N′-dithiobisamines and hydrogen sulfide.—The ready interaction of hydrogen sulfide and thiols with N,N′-dithiobisamines suggests a novel method of olefinic sulfuration. Reaction of 2-methylpent-2-ene with N,N′-dithiobismorpholine at 20° and 65° was not effected by catalytic amounts of hydrogen sulfide but required molar quantities of this agent, and then negligible sulfuration of the olefin occurred. Boiling cyclohexene gave similar results. However, 2,6-dimethylocta-2,6-diene with N,N′-dithiobismorpholine and hydrogen sulfide at 140° gave in 1 hour morpholine and a high yield of largely saturated, sulfurated product, in which the ratio of crosslinked polysulfide to cyclic sulfide was considerably greater than was observed for the comparable reaction with sulfur[12] or with sulfur and diethylamine[1]. No detailed analysis of the cyclic sulfide fraction was attempted but the presence of ca. 26% of the thiophan (I) was indicated by infrared spectroscopy. The poly-



(I) (II) (III)

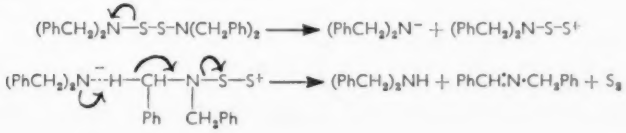
sulfide was mainly saturated, its infrared spectrum being similar to that of compound (II), suggesting that the polysulfide (III) was the major component as similarly obtained from the diene-sulfur-diethylamine reaction[1]. This was confirmed by hydrogenolysis of the polysulfide with lithium aluminum hydride, a thiol similar to (III) being obtained.

Mechanism of the decomposition of N,N′-dithiobisamines.—The formation of amine (R_2NH) by reaction of N,N′-dithiobisamines, $R_2N{\cdot}S_2{\cdot}NR_2$, with reagents of the type HX (X = Cl, SO_3H, SH, SR′) indicates that fission of the N—S bond is an important reaction of this type of compound, e.g.:



When HX is a thiol the products are amine and tetrasulfide, but when it is hydrogen sulfide the initially formed H_2S_4 probably forms the salt $R_2NH_2^+HS_4^-$ which decomposes further, particularly in a polar solvent or on treatment with acid, to give sulfur and $R_2NH_2^+HS^-$, as observed experimentally.

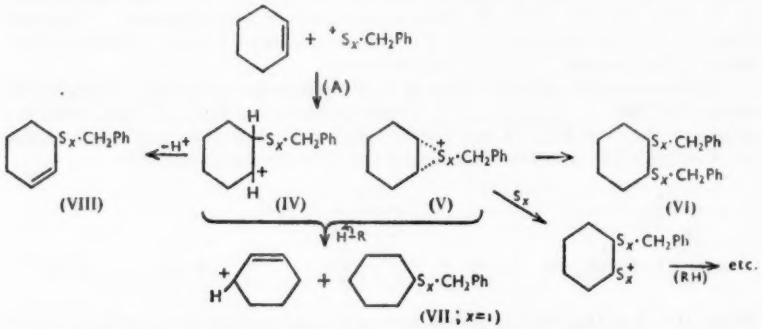
The thermal decomposition of N,N′-dithiobisdibenzylamine to dibenzylamine, hydrogen sulfide, and N-benzyl(thiobenzamide) may be explained similarly as involving initial heterolysis of the N—S bond followed by elimination, thus:



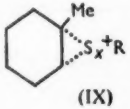
Formation of hydrogen sulfide and N-benzylthiobenzamide is then regarded as resulting from (*a*) reaction of the dibenzylamine with sulfur (cf. Moore and Saville[1]), and (*b*) reaction of the benzylidenebenzylamine with sulfur. Although the presence of the Schiff's base in the products could not be proved, support for its formation as an intermediate includes (i) the formation of thioamides from Schiff's bases and sulfur[13], and (ii) the isolation of Schiff's bases in sulfur-amine reaction products[14].

Isolation of N,N′-trithiobisdibenzylamine on reaction of the dithiobisamine with cyclohexene at 140° points to disproportionation involving S—S bond fission as an alternative to some extent to N—S fission. Comparable reactions have been observed with substituted thiuram disulfides, $R_2N \cdot CS \cdot S \cdot S \cdot CS \cdot NR_2$.

Mechanism of olefinic sulfuration with N,N′-dithiobisdibenzylamine.—Unlike the reaction of N,N′-thiobisdiethylamine with cyclohexene[1] that of N,N′-dithiobisdibenzylamine with olefins yields products which result mainly from the addition of benzylthio-groups to olefinic double bonds, indicating an anomalous course for olefinic sulfuration. The reactions which lead to the formation of the benzylthio-groups remain obscure, but the observed products may result from the electrophilic attack of benzylthio- or benzyl-polythio-cations, $Ph \cdot CH_2 \cdot S_x^+$, on the olefin. Thus the major products obtained from cyclohexene, viz., benzyl cyclohexyl sulfide and the polymer $Ph \cdot CH_2 \cdot S_x \cdot C_6H_{10} \cdot S_x \cdot CH_2Ph$ (IV; x = mainly 1), may be formed as shown in the annexed scheme. The intermediate formed from the initial reaction (A) may be assigned either a classical cationic structure (IV) or a π-complex structure (V). Cyclic sulfonium ions of type (V) (cf. Bartlett and Swain[16]) were regarded by Lien, McCaulay, and



Proell[17] as chain carriers for the formation of compounds analogous to the polysulfides (VI) in acid-catalyzed reaction of disulfides with olefins, and participation of such intermediates in the present reaction is in conformity with recent mechanistic studies of olefin-sulfur reactions[18]. Formation of the monosulfide (VII) is represented as involving hydride-ion transfer between olefin and (IV–V)[18], which is well known in the analogous Friedel-Crafts reactions[19]. The isolation of a little cyclohex-2-enethiol on hydrogenolysis of the polymeric



(IX)

fraction (*b*) suggests that a polysulfide (VIII) may be a minor product, formed as shown.

The corresponding reaction of the dithiobisamine with 1-methylcyclohexene recalls the isolation of 1-methylcyclohexyl phenyl sulfide on reaction of diphenyl tetrasulfide with 1-methylcyclohexene[20]. It is believed that these reactions follow the pattern suggested for cyclohexene proceeding *via* the intermediate sulfonium ion (IX) and leading mainly to tertiary C—S compounds.

Mechanism of olefinic sulfuration with dithiobismorpholine and hydrogen sulfide.—Since negligible reaction occurs at 140° between dithiobismorpholine and cyclohexene or 2,6-dimethylocta-2,6-diene, the ready sulfuration of the diene in the presence of hydrogen sulfide must be due to reaction of the dithiobisamine with hydrogen sulfide. The active sulfurating agent appears to be $C_4H_8ONH_2^+ \cdot HS_4^-$ and the mechanism of sulfuration is probably analogous to that in the amine-sulfur-olefin systems[1].

The formation of amines by reaction of hydrogen sulfide and thiols with dithiobisamines has been used to confirm the belief[21] that hydrogen sulfide and thiols are not intermediates in sulfur-olefin reactions. It was found that cyclohexene and sulfur at 140° in the presence of dithiobismorpholine yield the normal olefinic polysulfide obtained also in the absence of the dithiobisamine and that morpholine formation is negligible.

EXPERIMENTAL

Preparation of N,N′-dithiobisamines.—N,N′-Dithiobisdibenzylamine, obtained (92%) from dibenzylamine and sulfur monochloride by Throdahl and Harman's method[22], crystallized from alcohol-light petroleum in pale yellow needles, m.p. 79–80° (Found: C, 73.5; H, 6.1; N, 6.05. $C_{28}H_{28}N_2S_2$ requires C, 73.7; H, 6.1; N, 6.1%). N,N′-*Dithiobismorpholine* was obtained similarly (82%) as colorless needles [from ethanol-ethyl acetate (10:1),] m.p. 125° (Found: S, 27.0. Calc. for $C_8H_{16}O_2N_2S_2$: S, 27.1%). N,N′-*Dithiobis-(β-ethylaminopropionitrile*) was obtained (66%) by Harman's method[23] as colorless prisms (from ethanol-acetone), m.p. 77–79° (Found: C, 46.8; H, 6.85; N, 21.2. Calc. for $C_{10}H_{18}N_4S_2$: C, 46.5; H, 7.0; N, 21.7%).

Preparation of reference compounds.—N-Benzyl(thiobenzamide), m.p. 84–85° (Found: C, 73.8; H, 5.75; N, 6.2. Calc. for $C_{14}H_{13}NS$: C, 74.0; H, 5.7; N, 6.2%), was prepared in 52% yield by reaction of N-benzylbenzamide (10 g) with phosphorus pentasulfide (5 g) in boiling xylene. It was recovered unchanged after 10 hr at 140° *in vacuo*; it was not hydrolyzed by dilute mineral acids, but in refluxing sulfuric acid (70% w/w) (1 hr) gave benzoic acid, m.p. and mixed m.p. 120–121°, and benzylamine, isolated as the picrate, m. p. and mixed m.p. 193–194°.

Cyclohex-2-enethiol, obtained (69%) from 3-bromocyclohexene and thiourea, had b.p. 44°/11 mm, n_D^{25} 1.5230 (Found: C, 63.65; H, 8.8; S, 27.35; SH, 28.4. $C_6H_{10}S$ requires C, 63.2; H, 8.8; S, 28.0; SH, 29.0%). It gave the *2,4-dinitrophenyl derivative* as yellow prisms (from ethanol-acetone), m.p. 114–115° (Found: C, 51.55; H, 4.6; N, 10.05. $C_{12}H_{12}O_4N_2S$ requires C, 51.4; H,4 .3; N, 10.0%).

Thiophenol (11 g, 0.1 mole) was added with stirring to a solution of sodium (2.3 g, 0.1 g-atom) in ethanol (40 ml) under nitrogen, followed by 3-bromocyclohexene (16.1 g, 0.1 mole) in ethanol (15 ml). After being warmed for 30 min the mixture was poured into water, and extracted with ether, and the extract was washed with water, dried (K_2CO_3), and fractionated, to give *cyclohex-2-*

enyl phenyl sulfide, b. p. 89–90°/0.01 mm., n_D^{30} 1.5920 (79%) (Found: C, 75.35; H, 7.3; S, 16.65. Calc. for $C_{12}H_{14}S$: C, 75.8; H, 7.4, S; 16.8%).

Phenylcyclohexyl sulfide, b.p. 11°/0.1 mm, n_D^{25} 1.5680, was prepared by Cunneen's method[24]. The corresponding sulfone had m.p. 73–74°.

Cyclohexene (15 g), toluene-ω-thiol (30 g), and ascaridole (0.1 g) were refluxed on the steam bath for 7 hr and the product was fractionated, to give benzyl cyclohexyl sulfide, b. p. 88–89°/0.01 mm, n_D^{25} 1.5556 (45%) (Found: C, 75.4; H, 8.7; S, 15.4. Calc. for $C_{13}H_{18}S$: C, 75.7; H, 8.7; S, 15.6%), which with peracetic acid gave the sulfone, colorless flakes from (ethanol-light petroleum), m. p. 100–101° (Found: C, 65.4; H, 7.55; S, 13.25. Calc. for $C_{13}H_{18}O_2S$: C, 65.5; H, 7.5; S, 13.4%).

Attempts to prepare 1,2-*epithiocyclohexane* from 1-chloro-2-thiocyanatocyclohexane and sodium sulfide[25] gave mainly a polymer, as expected for the alkaline conditions used[26], and a thiol. Reduction of the polymer with lithium aluminum hydride gave the same thiol, b. p. 48–50°/0.1 mm, n_D^{30} 1.5410 (Found: C, 51.1; H, 8.25; S, 37.1. Calc. for $C_6H_{12}S_2$: C, 48.6; H, 8.1; S, 43.2%), which contained cyclohexane-1,2-dithiol since on reaction with benzaldehyde and hydrogen chloride it gave the dithiolan[27], m. p. 115°, and with potassium methyl xanthate gave the *cyclohexyl trithiocarbonate*[28], m. p. 169°. Attempts to prepare a solid 2,4-dinitrophenyl sulfide derivative of the dithiol were unsuccessful.

Benzyl 1-methylcyclohexyl sulfide was prepared by Moore and Saville's method[1]. On oxidation with peracetic acid it gave the *sulfone* as flakes [from light petroleum-ethanol (10:1)], m. p. 100° (Found: C, 67.1; H, 8.0; S, 12.6. $C_{14}H_{20}O_2S$ requires C, 66.7; H, 7.9; S, 12.7%).

Chemical decompositions of N,N'-dithiobisamines.—N,N'-Dithiobisdibenzylamine (2.0 g) was shaken vigorously with 15% sulfurous acid (50 ml) and then cooled to 0° for 2 days. The S_4-*compound* separated (2.7 g) and formed colorless prisms, m. p. 143–144°, from ethanol (Found: C, 53.55; H, 5.0; N, 4.25; S, 20.45. $C_{28}H_{32}N_2O_6S_4$ requires C, 54.2; H, 5.15; N, 4.5; S, 20.7%).

The same *N,N'-dithiobisamine* was decomposed by warm dilute mineral acids to sulfur, hydrogen sulfide, sulfur dioxide, and the parent amine, identified as picrate.

A benzene solution of the N,N'-dithiobisamine with hydrogen sulfide gave a red insoluble oil and sulfur; the decomposition was favored by the presence of polar solvents.

N,N'-Dithiobismorpholine (11.8 g, 0.05 mole) and toluene-*p*-thiol (12.4 g, 0.1 mole) were mixed as fine powders at room temperature: a rapid reaction ensued, the mixture becoming yellow, liquid, and finally deep red, with the evolution of a small amount of hydrogen sulfide. After 3 hr the product was fractionated to give morpholine (5.8 g), b. p. 25–30°/10 mm, n_D^{30} 1.4560 (identified as picrate, m. p. 146–147°), and a residual yellow oil (14.9 g), undistillable at 140°/0.01 mm, which was devoid of thiol and appeared to be principally di-*p*-tolyl tetrasulfide (13.2 g) (Found: C, 53.05; H, 4.7; S, 40.65. Calc. for $C_{14}H_{14}S_4$: C, 54.2; H, 4.5; S, 41.3%). Use of a solvent (e.g., ethanol) gave a more controllable reaction and minimized side reactions leading to hydrogen sulfide. Other thiols reacted similarly. Comparable reactions between sulfenamides and thiols were less vigorous owing to the intermediate formation of the solid amine-thiol salt.

N,N'-Dithiobisdibenzylamine (9.1 g, 0.02 mole) was unchanged when refluxed for 2 hr with lithium aluminum hydride (1.9 g, 0.05 mole) in ether (200 ml). The N,N'-dithiobisamine (9.1 g) in tetrahydrofuran (20 ml) was

then refluxed for 4 hr with the reagent (3.0 g) in tetrahydrofuran (50 ml). Decomposition with ice and 2n-sulfuric acid gave hydrogen sulfide and a white solid (apparently dibenzylammonium sulfate) which was treated with alkali to yield dibenzylamine, isolated as its hydrochloride (4.5 g equiv. to 3.8 g of amine). The original ether extract gave only impure sulfur ($\gtrsim$0.8 g). The starting material was stable to cold 2n-sulfuric acid.

[With Dr. G. H. Thomas].—(i) A mixture of N,N′-dithiobismorpholine (3.0 g) and methyl *iso*thiocyanate (2.5 g) in benzene (20 ml) was heated *in vacuo* for 8 hr at 140°, giving sulfur and *di-(α-methylimino-α-morpholinomethyl) sulfide*, prisms (from ethanol), m. p. 150–151° Found: C, 50.45; H, 7.9; N, 20.0; S, 11.55. $C_{12}H_{22}O_2N_4S$ requires C, 50.3; H, 7.7; N, 19.6; S, 11.2%). (ii) A comparable reaction to (*i*), with benzyl *iso*thiocyanate, gave *di-(α-benzylimino-α-morpholinomethyl) disulfide*, plates (from benzene), m. p. 98° (Found: C, 61.1; H, 6.8; N, 11.95; S, 13.35. $C_{24}H_{30}O_2N_4S_2$ requires C, 61.3; H, 6.4; N, 11.9; S, 13.6%).

Thermal decomposition of N,N′-dithiobisdibenzylamine.—(i) When this compound, m. p. 80°, was heated under nitrogen for 5 hr at 140° no hydrogen sulfide was evolved and the product (Found: C, 73.55; H, 6.15%) had m. p. and mixed m. p. with the original compound, 70–71°, indicating possible disproportionation. (ii) The dithiobisamine (5.0 g) was heated *in vacuo* for 20 hr at 140° ± 1°: hydrogen sulfide was formed, together with N-benzyl(thiobenzamide) (2.1 g), m. p. 83–84° (Found: C, 74.2; H, 6.1; N, 6.2. Calc. for $C_{14}H_{13}NS$: C, 74.0; H, 5.7; N, 6.2%). (iii) The dithiobisamine (9.1 g) was heated in nitrogen for 24 hr at 140° ± 1°, then treated in ether with hydrogen chloride, to give dibenzylammonium hydrochloride. Evaporation of the solution gave N-benzyl-(thiobenzamide) (6.1 g), m. p. 81–83° (Found: C, 74.1; H, 5.7; N, 6.2%).

Reaction of dibenzylamine with sulfur.—The amine (10.3 g) and sulfur (2.0 g) were heated *in vacuo* for 24 hr. at 140° ± 1° with shaking, then cooled to −10° for 2 days. *N-Benzylthiobenzamide* (4.2 g), m. p. and mixed m. p. 84–85° (Found: C, 73.7; H, 5.9; N, 6.4%), separated. Evaporation of the filtrate gave *dibenzylammonium hydrogen sulfide*, m. p. (sealed tube) 32—34° (cf. Achterhof[29]).

Thermal decomposition of N,N′-dithiobis-(α-ethylaminopropionitrile).—Heating the compound *in vacuo* for 10 hr at 140° ± 1° gave traces of the *hydrogen sulfide* of *β-ethylaminopropionitrile* and a tar.

Reaction of α-ethylaminopropionitrile with sulfur.—Heating the amine (9.8 g) with sulfur (3.2 g) *in vacuo* for 10 hr at 140° ± 1° gave the *amine hydrogen sulfide* and tar.

Reaction of N,N′-dithiobisdibenzylamine with cyclohexene.—(1) The dithiobisamine (34.2 g, 0.075 mole) and the olefin (61.5 g, 0.75 mole) were heated *in vacuo* for 24 hr at 140° ± 1°. The red-brown liquid yielded no crystals at −10° (1 week). Unchanged olefin (36 g.) was removed and to the residue was added light petroleum (250 ml). A dark oil (~5 g) separated, which crystallized at low temperature, the solid product being *N-benzyl(thiobenzamide)*, obtained as light yellow needles on repeated crystallization (charcoal) from aqueous ethanol (m. p. and mixed m. p. 82–83.5°) (Found: C, 73.5; H, 5.75; N, 6.1%). Treatment of the petroleum solution with 2n-hydrochloric acid (150 ml) gave dibenzylammonium hydrochloride (12.0 g). This was removed, and the filtrate re-extracted with acid, washed with water, dried ($CaCl_2$), and evaporated, to give the olefinic sulfuration product (i) (33 g) (Found: C, 72.65; H, 7.55; N, 1.3%; C: H, 6: 7.5). Fractional distillation of this gave (ii) 2,4-dinitrotoluene, m. p. 70° (ca. 1 g), (iii) a liquid, b. p. 88°/0.001 mm., n_D^{25} 1.5500

(5.7 g) (Found: C, 73.7; H, 9.0; N, 0.07; S, 17.15%), and (iv) a deep red oil (15.3 g), undistillable at 140°/0.001 mm. (Found: C, 71.0; H, 6.85; N, 1.89%) which at 0° slowly deposited a trace of N-benzyl(thiobenzamide).

Infrared spectroscopic analysis of fraction (iii) showed that the principal constituent (70%) was *benzyl cyclohexyl sulfide*, by comparison with a synthetic sample. Refractionation gave (iii*a*) b. p. 78–80°/0.01 mm, n_D^{25} 1.5470 (4.0 g) (Found: C, 74.0; H, 9.25; S, 16.2%; C: H, 6: 9), and (iii*b*) b. p. 82–86°/0.01 mm, n_D^{25} 1.5665 (0.8 g) (Found: C, 71.35; H, 8.65; S, 19.6%; C: H, 6: 8.7). Infrared analysis of fractions (iii*a* and *b*) revealed *benzyl cyclohexyl sulfide* as the main component, only small amounts of *dicyclohexyl* and *dicyclohex-2-enyl sulfide* being present. The presence of benzaldehyde in fractions (iii) and (iii*a* and *b*) was established by a band at 1710 cm^{-1} due to C=O in their infrared spectra, and by formation of benzaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 234–235°. Oxidation of fraction (iii) with peracetic acid gave *benzyl cyclohexyl sulfone*, m. p. and mixed m. p. 100–101° (Found: C, 65.3; H, 7.55; S, 13.6. Calc. for $C_{13}H_{18}O_3S$: C, 65.5; H, 7.5; S, 13.4%). No other crystalline sulfone could be identified.

Extraction of a benzene solution of fraction (iv) with 10% sulfurous acid failed to give any S_4-derivative, indicating the absence of the dithiobisamine. [In an independent experiment, treatment of a benzene solution of the dithiobisamine with 10% sulfurous acid gave the S_4-compound (93%).] The benzene solution of fraction (iv) was washed with aqueous sodium hydrogen carbonate, then with water, dried, and eluted through alumina, to give fraction (v) (Found: C, 66.9; H, 6.15; N, 1.8; S, 25.2%; C: H, 6: 6.6). A solution of this fraction (14.0 g) was refluxed with stirring with lithium aluminum hydride (5.0 g) in ether (250 ml) for 2 hr, then decomposed with ice and 2*n*-sulfuric acid. Removal of the solvent and fractionation gave: (v*a*) impure *cyclohex-2-enethiol*, b. p. 40°/10 mm, n_D^{25} 1.5070 (0.5 g) (Found: C, 62.75; H, 9.2; S, 26.6; SH, 28.8%; C: H, 6: 10.5. Calc. for $C_6H_{10}S$: C, 63.2; H, 8.8; S, 28.0; SH, 29.0%) (its infrared spectrum indicated >40% of the thiol; it gave *2,4-dinitrophenyl cyclohex-2-enyl sulfide* (m. p. 115°, mixed m. p. 114–115°); (v*b*) b. p. 60–80°/10 mm, n_D^{25} 1.5460 (2.1 g) (Found: C, 65.8; H, 7.6; S, 25.35%; C: H, 6:8.4) [shown by infrared analysis to contain toluene-ω-thiol (70%) identified as its 2,4-dinitrophenyl derivative, m. p. and mixed m. p. 128–129° (Found: C, 53.4; H, 3.45; N, 9.4. Calc. for $C_{13}H_{10}O_4N_2S$: C, 53.8; H, 3.45; N, 9.7%); the presence of cyclohexanethiol was demonstrated by the formation of 2,4-dinitrophenyl cyclohexyl sulfide, m. p. and mixed m. p. 145.5–147°]; (v*c*) b. p. 35°/0.01 mm, n_D^{25} 1.5645 (1.1 g) (Found: C, 59.65; H, 7.4; S, 32.25%; C: H, 6: 8.9) [shown by infrared analysis to consist mainly of benzyl cyclohexyl sulfide (or material of the type $Ph \cdot CH_2 \cdot S \cdot C_6H_{10} \cdot S \cdot CH_2Ph$) together with toluene-ω-thiol, identified as the 2,4-dinitrophenyl derivative, m. p. and mixed m. p. 125–127° (Found: C, 53.45; H, 3.5; N, 9.8%), and a cyclohexanedithiol of unknown composition characterized as its bis-2,4-dinitrophenyl derivative, m. p. 193–194.5° (Found: C, 45.5; H, 3.45; N, 11.35. Calc. for $C_{18}H_{16}O_8N_4S_2$: C, 45.1; H, 3.34; N, 11.7%)]; (v*d*), b. p. 84–88°/0.01 mm, n_D^{25} 1.5590 (0.65 g) (Found: C, 69.1; H, 8.4; S, 21.8%; C: H, 6: 8.7) [shown by infrared analysis to be mainly benzyl cyclohexyl sulfide and $Ph \cdot CH_2 \cdot S \cdot C_6H_{10} \cdot S \cdot CH_2Ph$, but containing also a cyclohexanedithiol characterized as its bis-2,4-dinitrophenyl derivative, m. p. 195–196°]; and (v*e*) a residue (7.8 g) undistillable at 140°/0.001 mm. Chromatography of (v*e*) (7.0 g) in light petroleum gave (v*f*) a light yellow oil (1.8 g) [Found: C, 74.1; H, 7.65; N, 1.35%; C: H, 6: 7.4; *M* (ebullioscopic in C_6H_6), 294, 303)], and further elution with light petroleum-ethanol

(19:1) gave (*vg*) a yellow oil (4.0 g] [Found: C, 78.75; H, 7.35; N, 3.0%; C: H, 6:7; *M* (as above), 362, 372]. Infrared examination of fractions (*vf* and *g*) indicated the presence of benzyl and cyclohexyl groups suggestive of the presence of $Ph \cdot CH_2 \cdot S \cdot C_6H_{10} \cdot S \cdot CH_2Ph$ and apparently traces of *N*-benzyl(thiobenzamide), but definitely precluded the presence of tetrabenzylhydrazine.

(2) Reaction of *N,N'-dithiobisdibenzylamine* (22.8 g) with *cyclohexene* as above gave a fraction (0.65 g) which was almost pure benzylamine, b. p. 35°/0.2 mm, n_D^{20} 1.5425 (Found: C, 78.15; H, 8.4; N, 12.5; S, 1.0. Calc. for C_7H_9N: C, 78.5; H, 8.4; N, 13.0%), identified as its picrate, m. p. 198–199° (Found: C, 46.25; H, 3.5; N, 16.9. Calc. for $C_{13}H_{12}O_7N_4$: C, 46.4; H, 3.6; N, 16.7%).

(3) The dithiobisamine (17.1 g) and olefin (36.9 g) were heated *in vacuo* for 10 hr at 140° ± 1°. The product, which contained no tar, was freed from volatile material, and the residue (20.7 g) cooled to 0°: it partially crystallized. Filtration gave a solid (10.1 g) which crystallized from light petroleum (charcoal) in prisms, m. p. 72–73° (Found: C, 71.05; H, 5.8; N, 5.65%). Fractionation from light petroleum then gave *N,N'-trithiobisdibenzylamine* as prisms (from light petroleum or ethanol-ethyl acetate), m. p. 109–111° (Found: C, 68.85; H, 5.7; N, 5.37; S, 19.5. $C_{28}H_{28}N_2S_3$ requires C, 68.8; H, 5.7; N, 5.7; S, 19.7%). Examination of the more soluble fractions failed to yield any N,N'-monothiobisdibenzylamine.

Reaction of N,N'-dithiobisdibenzylamine with 1-methylcyclohexene.—A similar procedure to that followed in the cyclohexene reaction was used. The main experimental findings are summarized on p. 578.

Formation of morpholine from 2-methylpent-2-ene, N,N'-dithiobismorpholine, and hydrogen sulfide.—General procedure. The N,N'-dithiobisamine (5.9 g, 0.025 mole) and the olefin (0.25 mole) were stirred rapidly at 20° or 65° for 1 hr while either a trace or a steady stream of hydrogen sulfide was introduced. After removal of solid N,N'-dithiobisamine and/or sulfur, the solution was freed from olefin and the residue fractionated or titrated directly in aqueous ethanol against standard hydrochloric acid to determine the yield of morpholine (identified as its picrate) (see table). In two control experiments the olefin was replaced by ethanol and by light petroleum.

Expt. no.	1	2	3	4	5	6	7
Olefin	†	†	†	0	0	†	†
H_2S	0	Tr	†	†	†	Tr	†
Temp.	65°	65°	65°	65°	65°	20°	20°
Other solvent	—	—	—	Pet	EtOH	—	—
Yield (g) of morpholine	0.0	0.1	2.8	0.67	1.3	0.4	0.4
N,N'-Dithiobisamine recovered (g)	5.6	5.45	—	—	—	—	—

† = Excess. Tr = trace. Pet = light petroleum.

Reaction of 2,6-dimethylocta-2,6-diene with N,N'-dithiobismorpholine in absence and in presence of hydrogen sulfide.—(1) The olefin (25.0 g) and the dithiobisamine (12.6 g), refluxed under nitrogen for 1 hr at 140°, gave a reddish-brown product, with no indications of amine hydrogen sulfide or of hydrogen sulfide formation. On cooling, unchanged dithiobisamine (8.8 g) separated. Filtration and washing the filtrate with ice-cold light petroleum gave further dithiobisamine (1.8 g, total 85%).

(2) A stirred mixture of the olefin (25.0 g) and the dithiobisamine (12.6 g) was refluxed under nitrogen at 140° and hydrogen sulfide introduced during 1 hr. Morpholine hydrogen sulfide separated. The reddish-brown product was decanted from tar (2 g) and fractionated to give fractions: (i) b. p. 36–50°/10

mm, n_D^{20} 1.4525 (6.5 g) (Found: C, 54.9; H, 10.9; N, 11.43%), containing morpholine (picrate, m. p. 146–147°); (ii) b. p. 60–80°/10 mm, n_D^{20} 1.4535 (16.8 g) (Found: C, 86.75; H, 10.85; N, 1.35%; C: H, 10: 18), unchanged olefin containing a little morpholine (picrate, m. p. 146–147°); (iii) unchanged olefin plus cyclic sulfide, b. p. 89–92°/10 mm, n_D^{20} 1.4870 (0.9 g) (Found: C, 77.0; H, 11.5; N, 0.07%; C: H, 10: 18); (iv) evaporative distillate (1.7 g) (Found: C, 56.1; H, 8.4; N, 0%; C: H, 10: 18); (v) residue (5.0 g) which on elution in benzene through alumina and removal of solvent gave a polysulfide (Found: C, 49.4; H, 7.45; N, 0.01%; C: H, 10: 18). Infrared analysis confirmed the presence of morpholine and unchanged olefin in fractions (i) and (ii) and revealed the presence of ~26% of CH_2:CRR′ in (iii) indicative of the cyclic sulfide; fraction (iv) contained R·CH:CRR′ groups (band at 830 cm^{-1}) but the major polysulfide fraction (v) was saturated (compound III). Fraction (v) showed no absorption maximum near 4000 A, the absorption being consistent with that of a saturated polysulfide. A portion (4.0 g) of fraction (v) in ether was reduced with lithium aluminum hydride (1.5 g) in the usual manner and the product fractionated to give materials: (v*a*) b. p. 60°/0.1 mm, n_D^{20} 1.5110 (0.7 g) (Found: C, 61.8; H, 10.1; S, 27.5; SH, 20.3%; C: H, 10: 19.6); (v*b*) b. p. 78–80°/0.1 mm, n_D^{20} 1.5275 (0.9 g) (Found: C, 56.85; H, 9.45; S, 28.9; H, 25.2%; C: H, 10: 20); and (v*c*), a residue, which on elution in light petroleum (b. p. 40–60°) through alumina gave a polysulfide as an orange-red oil (Found: C, 58.05; H, 9.6; S, 28.8; C: H, 10: 19.8. Calc. for $C_{20}H_{40}S_4$: C, 58.8; H, 9.8; S, 31.4%). The infrared spectra of (v*a* and *b*) showed strong resemblances to that of the thiol-cyclic sulfide (II), (v*a*) containing also traces of unsaturated material; the infrared spectrum of (v*c*) was similar to those of (v*a* and *b*).

Influence of N,N′-dithiobismorpholine on the sulfur-cyclohexene reaction.—*cyclohexene* (41 g, 0.5 mole), sulfur (4.8g, 0.15 g-atom), and the dithiobisamine (11.8 g, 0.05 mole) were heated *in vacuo* for 5 hr at 140° ± 1°. The deep red liquid product was decanted from tar (1 g) and fractionated to give: (i) impure morpholine, b. p. 40°/10 mm, n_D^{20} 1.4600 (0.6 g) (Found: C, 56.3; H, 10.6; N, 14.4. Calc. for C_4H_9ON: C, 55.2; H, 10.35; N, 16.1%; (ii) dithiobisamine, b. p. 60°/0.001 mm. (1.2 g); and (iii) a residue (16 g) which was extracted from benzene, with 0.1 *n*-hydrochloric acid, washed with water, extracted with sulfurous acid, washed, dried, eluted through alumina, and fractionated to give a polysulfide (10.5 g) containing a trace of the dithiobisamine (Found: C, 53.45; H, 7.0; N, 0.5%; C: H, 6: 9.4).

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SYNOPSIS

N,N′-Thiobisamines, $(RR'N)_2S_x (x > 1)$, undergo N—S bond fission in the presence of hydrogen sulfide, thiols, and other polar reagents. On thermal decomposition at 140° they give the parent amine, hydrogen sulfide, and thioamides, R·NH·CS·R″. N,N′-Dithiobisdibenzylamine with cyclohexene at

140° gives a complex mixture of mainly saturated sulfides and polymeric sulfides containing benzyl and cyclohexyl groups, together with N-benzyl-(thiobenzamide) and dibenzylamine. A novel method of olefinic sulfuration with the thiobisamines and hydrogen sulfide is described and the effect of the thiobisamines on interaction of sulfur and olefin is examined. Mechanisms of the thermal decomposition and of the reactions with olefins are discussed.

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THE MECHANISM OF SULFUR REACTION IN THE POLYMERIZATION OF CHLOROPRENE AND OF THIURAM REACTION IN THE DEGRADATION AND STRUCTURIZATION OF POLYCHLOROPRENE *

A. L. KLEBANSKIĬ, N. JA. ZUKERMAN,

AND L. P. FOMINA

S. V. LEBEDEV ALL-UNION SYNTHETIC RUBBER RESEARCH INSTITUTE, LENINGRAD, USSR

In the preparation of chloroprene polymers sulfur, in addition to tetraethylthiuram disulfide (TETD), is used as a modifier. This problem was discussed in a paper by Mochel and others[1] who explained the effect of sulfur and TETD upon the basis of copolymerization processes with S_x as comonomer. There is formed a macromolecule consisting of polychloroprene fragments linked through sulfur:

$$-[CH_2-CCl=CH-CH_2]_n-S_x-[CH_2-CCl=CH-CH_2]_n-S_x\ldots$$

here $x = 2$–6. In this paper these concepts are developed further. Moreover, the paper illustrates the mechanism of reaction of thiurams in degrading and structurizing chloroprene polymers which are made in the presence of sulfur. As yet, this behavior has not been sufficiently explained in the literature.

THE POSSIBILITY OF SULFUR TERMINATION OF POLYMERIZATION OR OF SULFUR STRUCTURIZATION OF POLYMER

The kinetics of emulsion polymerization of chloroprene was studied to find if sulfur participates in terminating polymerization followed by combination of the radicals:

$$\ldots R\ldots S-S\cdot + \cdot S-S\ldots R \longrightarrow R-S-S\ldots S\ldots S\ldots R$$

The study showed that sulfur had no effect on the reaction rate (see Figure 1); in contrast to other polymerizations chloroprene polymerization is not inhibited by sulfur.

To see if sulfur adds to the double bonds of the polymer or reacts with α-methylenic hydrogens by substitution, the reaction in benzene solution of elemental sulfur with polychloroprene was studied. Polymer made in the absence of sulfur was used. The study was made in the presence or absence of initiators. The investigation established that heating the solution 40 hours at 40° C, or 8 hours at 100° C caused practically no addition of sulfur (see Table I). On the other hand during the polymerization process, sulfur combined with the polymer in substantial amounts.

* Translated by Henry J. Kehe from *Journal of Polymer Science*, Vol. 30, pages 363-374 (1958); presented at the Prague Symposium.

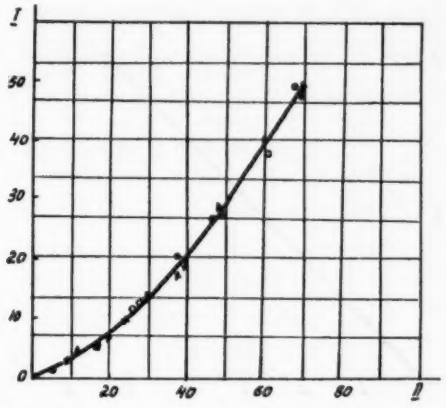


FIG. 1.—Emulsion polymerization of chloroprene. (I) Polymerization, %. (II) Time, minutes: (△) without sulfur; (O) 0.6% sulfur; (X) 0.9% sulfur.

Figure 2 shows that the amount of combined sulfur in the polymer increases proportionately to the amount charged; the average sulfur content can reach 4 and more weight per cent. As to the absence of structurization one may surmise that polymers of high sulfur content and low chloroprene content are completely soluble.

THE NATURE OF THE SULFUR LINKAGE IN POLYCHLOROPRENE

Sulfur linkages in polymers are more reactive than the carbon-carbon bonds. The sulfur to sulfur bond strength decreases proportionately to the increase in the number of sulfur atoms linked together. The bond strength depends on the electrostatic repulsion of the polar atoms and their increasing reactivity.

The investigation of the thermal decomposition in isopropylbenzene (cumene) solution of model compounds (I, II, III, IV) representing various

TABLE I

THE INTERACTION OF CHLOROPRENE AND POLYCHLOROPENE WITH SULFUR

Components	S, %	Initiator, %		Reaction conditions: t° C	Reaction conditions: Hours	Combined S in polymer, %
38% Chloroprene emulsion	0.7	Hyperis[a]	0.9	40	3	0.23
	1.0	Benzoyl peroxide	1.2	40	3	0.34
Chloroprene	6.0[b]	Benzoyl peroxide	1.0	40	72	2.25
Polychloroprene without sulfur	9.0	Benzoyl peroxide	1.0	40	40	0.030
	9.0	Benzoyl peroxide	1.0	100	8	0.025

[a] Cumene hydroperoxide.
[b] Sulfur introduced as a solution in carbon disulfide.

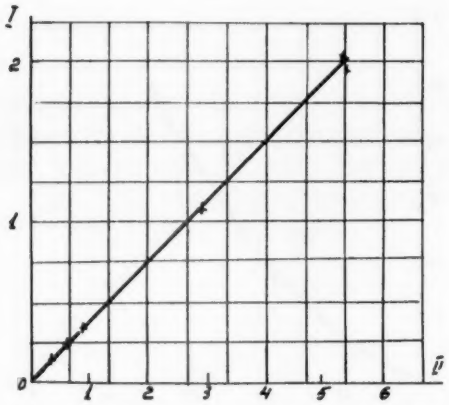


FIG. 2.—Relationship of final sulfur content in copolymers to sulfur content of starting materials. (I) Sulfur, %, in copolymer. (II) Sulfur, %, in starting materials.

forms of sulfur bonding in polychloroprene showed the following:

$$CH_2—CCl=CH—CH_2—S—CH_2—CH=CCl—CH_3 \quad (I)$$

$$CH_2—CCl=CH—CH_2—S—S—CH_2—CH=CCl—CH_3 \quad (II)$$

$$CH_2—CCl=CH—CH_2—S—S—S—S—CH_2—CH=CCl—CH_3 \quad (III)$$

$$CH_2—CCl=CH—CH_2—\underset{\downarrow}{S}—\underset{\downarrow}{S}—CH_2—CH=CCl—CH_3 \quad (IV)$$

In 8 hours at 145° C the decomposition of the disulfide (II) occurs to the extent of 24 per cent according to the following scheme:

$$R—S—S—R \longrightarrow 2RS\cdot$$

$$RS\cdot + H—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—C_6H_5 \longrightarrow RSH + C_6H_5—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\cdot$$

$$2C_6H_5—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\cdot \longrightarrow C_6H_5—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—C_6H_5$$

The decomposition of the tetrasulfide (III or IV) sets in even at 70° C and amounts to 2 per cent at this temperature in 8 hours.

The addition of an initiator, dinitrilazoisobutyric acid* (Dinitrilazoisobuttersaure), accelerates the rate 2 fold which confirms the radical chain mechanism. At 145° C the tetrasulfide decomposes completely in the course of 8 hours; thereby are formed primarily hydrogen sulfide—94 per cent, and disulfide—84 per cent according to the following equations (R_1 = radicals which

* Presumably, the authors mean azoisobutyrontrile; translator's and editor's note.

arise from the decomposition of the initiator; R=CH_3—CCl=CH—CH_2—):

$$R{-}S{-}S{-}S{-}\vdots{-}S{-}R + R_i \longrightarrow R{-}S{-}R_1 + R{-}S{-}S{-}S\cdot$$

$$R{-}S{-}S{-}S\cdot \longrightarrow R{-}S\cdot + \cdot S{-}S\cdot$$

$$R{-}S\cdot + R{-}S{-}\vdots{-}S{-}S{-}S{-}R \xrightarrow[(84\%)]{} R{-}S{-}S{-}R + R{-}S{-}S{-}S\cdot$$

$$R{-}S{-}S{-}S\cdot \longrightarrow R{-}S\cdot + \cdot S{-}S\cdot \text{ etc.}$$

$$\cdot S{-}S\cdot + 4H{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}C_6H_5 \longrightarrow 2H_2S + 4C_6H_5{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\cdot$$

$$2C_6H_5{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\cdot \longrightarrow C_6H_5{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}C_6H_5$$

$$RS\cdot + \cdot\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}C_6H_5 \xrightarrow[(10\%)]{} R{-}S{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}C_6H_5$$

The disulfide arises from the recombination of the radicals R—S· which, in part, combine with the cumyl radicals.

From this one may conclude that the type of sulfur bond in the chloroprene molecule is important in explaining the degradation and structurization processes in the polymers.

To determine the number of polysulfide units in the polymers, benzene solutions of them were shaken 70 to 100 hours with mercury. Because of insufficient stability of the diallylsulfide linkage and its tendency to isomerize, the analytical method was checked on compounds that might be considered as models for the chief structures of polychloroprene (compounds II, III, IV). It was found that sulfur was not removed from the disulfide by mercury. In contrast, mercury removes slightly more than one atom of sulfur from the tetrasulfide (by shaking for 70 hours at room temperature); this means that chiefly a trisulfide linkage remains.

Lengthening the treatment with mercury does not lead to further removal of sulfur. This agrees with the results of other investigators[2].

TABLE II

REMOVAL OF COMBINED SULFUR WITH MERCURY

	% Combined sulfur	Hours	Temp., °C	% Sulfur removed from combined sulfur
S—CH_2—CH=CCl—CH_2 / S—CH_2—CH=CCl—CH_2	26.6	Not removed by treatment		
S—S—CH_2—CH=CCl—CH_2 / S—S—CH_2—CH=CCl—CH_2	41.7	70	20	27
Polychloroprene	0.38	100	20	40
Polychloroprene	2.14	100	20	43

TABLE III

REDUCTIVE SPLITTING IN PRESENCE OF ZINC AMALGAM

	Hours	% S		η_{sp}/C		
		Combined	Removed (% of combined S)	Initial value	After reduction	After I_2 oxidation of the reduced polymer
S—S—CH_2—CH=CCl—CH_2 | S—S—CH_2—CH=CCl—CH_3	4	41.7	67	—	—	—
Polychloroprene	12	5.3	32	1.04	0.22	0.4

This method was applied to determining the number of polysulfide units in polymers. By this procedure, 40–43 per cent of the combined sulfur was removed. These results lead to the conclusion that in a given polymer of chloroprene the sulfur is present, on the average, as the pentasulfide; or, what may be more probable, as an equal mixture of tetra- and hexasulfide linkages (see Table II).

To answer the question about the distribution of the sulfur in the polymers, various methods were employed to break up the sulfur linkages by hydrogenolysis of the polymer in benzene solution: (a) effect of nascent hydrogen; (b) catalytic splitting with Raney nickel; or, (c), with lithium aluminum hydride. For comparative purposes, all of these methods were checked on the previously cited model compounds of di- and tetrasulfides. The trials showed that both were reduced to mercaptans by nascent hydrogen. Moreover, the excess of sulfur in the polysulfides appeared as hydrogen sulfide. As viscosity measurements show (Table III) a far reaching degradation takes place under the action of atomic hydrogen. The formation of mercaptans in the polymers was shown by treating the benzene solution of the reduced polymers with an iodine solution (warm). The viscosity measurements of a solution of polymers treated in this manner reveal thereby almost a doubling of η_{sp}/C values. This points to the presence of mercaptans that have formed from the reduction of the di- and polysulfide units in the starting polymers.

REDUCTION OF SULFUR LINKAGES WITH RANEY NICKEL

The reduction with Raney nickel takes place only in the presence of alcohol. One may assume that the mechanism of this reaction consists in the dehydro-

TABLE IV

REDUCTIVE CLEAVAGE OF SULFUR WITH RANEY NICKEL

	Hours	% S		η_{sp}/C values		Average molecular weight (viscometric)	
		Combined	Removed (% of combined S%)	Before reduction	After reduction	Before reduction	After reduction
S—CH_2—CH=CCl—CH_2 | S—CH_2—CH=CCl—CH_3	6	26.6	100	—	—	—	—
S—S—CH_2—CH=CCl—CH_2 | S—S—CH_2—CH=CCl—CH_3	6	41.7	100	—	—	—	—
Polychloroprene	16	0.47	77	0.80	0.45	130,500	59,000
Control experiment	16	0.47	—	0.80	0.78	130,500	125,000

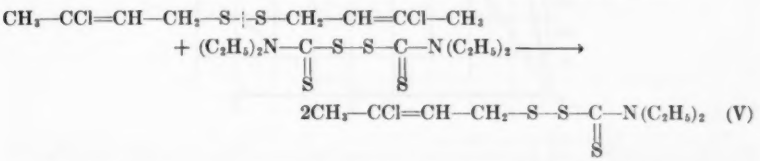
genation of alcohol under the influence of active nickel; thereby acetaldehyde and atomic hydrogen are formed. The latter brings about the reduction. These concepts are confirmed by the observation that in the absence of alcohol the simultaneous reduction and elimination occur only to a very limited extent.

The reductive degradation in the presence of Raney nickel was tested on the aforementioned model compounds in which the elimination of sulfur was completely realized through its reaction with hydrogen for six hours (Table IV).

The elimination of sulfur from the polymer proceeds much more slowly and only to the extent of 77 per cent. Simultaneously a degradation of the polymer takes place. The reductive elimination of sulfur from the polymers proceeds better with lithium aluminum hydride (86 per cent in 4 hours at 30° C). In the presence of either $LiAlH_4$ or Raney nickel the polychloroprene molecule may split into polymer fragments at the site of the sulfur groups. A comparison of the molecular weights of the individual fragments with the sulfur content in the starting material, calculated on one gram mole, should give the possibility of calculating the average number of sulfur atoms in the sulfide linkages.

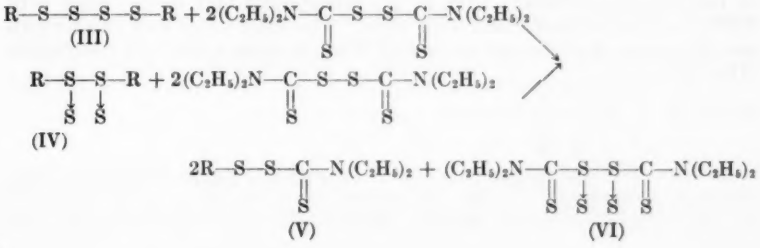
THE MECHANISM OF THE INTERACTION OF THIURAMS WITH CHLOROPRENE POLYMERS PREPARED IN THE PRESENCE OF SULFUR

The mechanism was explained through the use of the above cited compounds which served as models of the various types of sulfur linkages in polychloroprene molecules. The reaction of the disulfides with TETD was accomplished by heating them in benzene solution at 100° C (sealed tube). The single product (V) of this interaction formed in practically quantitative yield.



The interaction of the disulfide (II) with the thiuram proceeds at a greater rate than with isopropyl benzene (94 per cent of the disulfide reacts at 100° C in 8 hours). This observation makes it possible to draw the conclusion that in radical reactions thiuram is more active than isopropyl benzene.

The reaction of the tetrasulfide (III or IV) with TETD proceeds at 60°; both the tetrasulfide with chain structure (III) or with coordinately bound sulfur (IV) yield identical products (V and VI). Quantitative investigation permits writing the following equation:



where

$$R = CH_3—CCl=CH—CH_2—$$

One of the products is tetraethylthiuram tetrasulfide (TETtetra), crystals with a melting point of 106–7° C. On treatment with caustic (at 30° C) two atoms of sulfur are easily removed leading to the formation of tetraethylthiuram disulfide (TETD). The latter offers the chance to conjecture that two sulfur atoms are not in the chain, as Craig and Davidson proposed[3], but form a coordination compound with the molecule of TETD. This last view is based on a study of the kinetics of the removal of sulfur under the action of the caustic solution.

Figure 3 shows that the reaction of the tetrasulfide with TETD does not occur in the absence of peroxides (Curve *1*, Figure 3); only with the addition of 1 per cent of $K_2S_2O_8$ does a vigorous reaction set in (dashed Curve *2*, Figure 3). Increasing the concentration of $K_2S_2O_8$ greatly accelerates the reaction. The

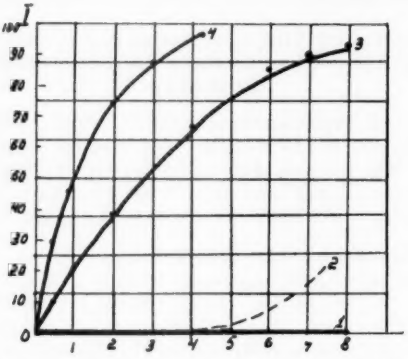


FIG. 3.—The effect of initiators on the rate of reaction of tetrasulfides with thiurams. (I) % Conversion of the tetrasulfides. (II) Time in minutes: (*1*) In absence of peroxides; (*2*) 1% $K_2S_2O_8$; (*3*) Peroxide of the tetrasulfides; (*4*) 3% $K_2S_2O_8$.

peroxides of the tetrasulfides themselves function in an analogous manner (Curve *3*). These results, and also the inhibition of the reaction by the action of PBNA (Neozone-D), confirm the radical mechanism of the interaction of tetrasulfides with thiurams.

In the reaction products of the tetrasulfide (III and IV) with TETD in the presence of caustic solution, TET tetra could not be detected. However, it was established that in the presence of alkali the reaction proceeds according to the following scheme. Initially the tetrasulfides (III or IV) react with TETD to form product V and TET tetra. The latter reacts with caustic with loss of 2 atoms of sulfur and forms TETD which again reacts with compounds III or IV:

$$2(C_2H_5)_2N—\overset{\overset{S}{\|}}{C}—\underset{\underset{S}{\downarrow}}{S}—\underset{\underset{S}{\downarrow}}{S}—\overset{\overset{S}{\|}}{C}—N(C_2H_5)_2 + 6NaOH \longrightarrow$$

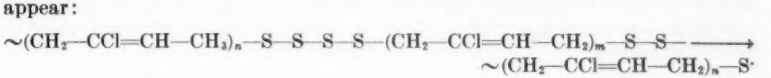
$$2(C_2H_5)_2N—\overset{\overset{S}{\|}}{C}—S—S—\overset{\overset{S}{\|}}{C}—N(C_2H_5)_2 + 2Na_2S + Na_2S_2O_3 + 3H_2O$$

All of these correlate with the phenomena that occur in the interaction of TETD with those polymers of polychloroprene obtained in the presence of sulfur. As known, TETD contributes to increase of plasticity and solubility of the polychloroprenes. Initiators, as peroxides and others, favor these; whereas, inhibitors delay these phenomena.

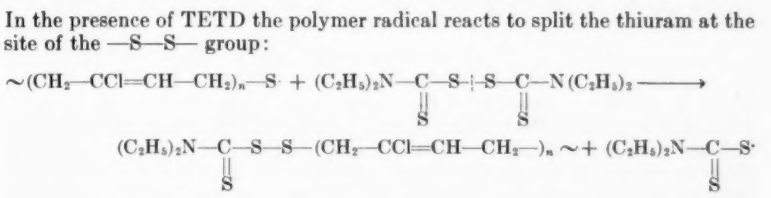
An increase in the pH of the latex promotes the action of TETD on the destructive degradation of the polymers. The velocity of this degradation depends on the presence of inhibitors which retard the effect of the thiuram. All of these confirm the radical mechanism of the reaction.

The fact that the increase in alkalinity accelerates the rate of the degradation of the polymers under the influence of thiuram does not contradict the indicated radical mechanism. The alkali, as given above, contributes to the conversion of the initial TET tetra into TETD; and in this way it accelerates the degradation of the polysulfide linkages in polymers. All of this finds agreement with the results which have been set forth for model systems.

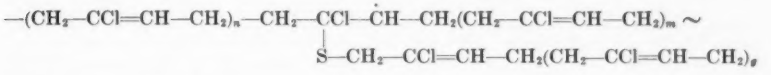
On the bases of these results which have been advanced for such systems, one may assume the following mechanism for the destructive degradation of chloroprene polymers. The polysulfide links in polychloroprene are subject easily to destruction under thermal action or peroxides, whereby free radicals appear:



In the presence of TETD the polymer radical reacts to split the thiuram at the site of the —S—S— group:



In absence of a thiuram the polymer radicals may react with the double bonds or the α-methylene groups of other polymer molecules with the consequence of branching and structuring of the macromolecule:



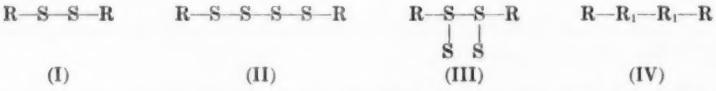
In the presence of a thiuram or other substances which are easily reactive with free radicals, the free valences at the end of or at an internal site of the molecule are broken off with simultaneous initiation of growth of the chain in linear as well as in a three dimensional direction.

The results of this investigation may also be used in explaining the vulcanization of natural or of various synthetic rubber with thiurams.

SUMMARY

To elucidate the mechanism of the reaction between chloroprene and sulfur, the following investigations have been carried out: (*1*) The reaction of a polychloroprene solution with sulfur under conditions of free radical initiation was

studied. It was found that sulfur does not react with polychloroprene, whereas under polymerization conditions the addition of sulfur proceeds readily. (*2*) A study of the polymerization of chloroprene monomer containing various amounts of sulfur (from 0.3 to 10%) showed that the sulfur content of the polymer increased in proportion to the amount of sulfur originally present. Polymers with a high sulfur content (3–5%) were found to be completely soluble at low degrees of polymerization. The latter finding indicates that the sulfur does not effect crosslinking, but that it is bound predominantly in a linear manner in the polymer chain. (*3*) The predominant form of bonding of the sulfur was found to be in di-and polysulfide linkages. The number of the latter increases with the sulfur content of the polymer. (*4*) By the action of nascent or catalytically activated hydrogen, the polymer was found to undergo extensive degradation with the loss of 80 to 100% of the bound sulfur and formation of low molecular weight polymer. In the course of the reduction the disulfide links are broken with the formation of polymer mercaptans, which are converted to disulfides by reaction with iodine; this is confirmed by an appropriate increase in the intrinsic viscosity. These findings confirm the copolymerization mechanism of the reaction between chloroprene and sulfur as proposed by Mochel and Nichols. (*5*) The mechanism of the degradation of polychloroprene sulfide by tetraethylthiuram disulfide (TETD) was studied by means of the following model systems, representing the main types of structures present in such polymers:



(I) (II) (III) (IV)

where R is $CH_3—CCl=CH—CH_2—$ and R_1 is $—CH_2—CCl=CH—CH_2—$. The radical nature of the reaction has been established and the correspondence between the results obtained with the model systems and the reactions taking place on treatment of polychloroprene sulfides with TETD has been demonstrated. Reaction schemes are proposed for the degradation and crosslinking of chloroprene polymers obtained in the presence of sulfur.

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A THEORETICAL STUDY ON THE MECHANISM OF ZIEGLER-TYPE POLYMERIZATIONS *

HEINZ UELZMANN

THE GENERAL TIRE & RUBBER CO., AKRON, OHIO

Since the discovery of catalysts for the polymerization of ethylene and α-olefins at low temperatures and low pressures by Ziegler[1] and coworkers, extensive experimental work has been done on this subject. Several theories on the mechanism of the catalysis have been discussed in order to illustrate the specific effects of different catalytic systems.

In this paper an attempt is being made to consolidate the existing theories into a single basic mechanism and to explain the numerous experimental facts from a different viewpoint. A theory on this subject must explain:

(1) An anionic propagation.
(2) A "hair-like" growth[2] of polyethylene from one active spot on the catalyst surface.
(3) Stereospecific polymerization of α-olefins and an exclusive head-to-tail arrangement according to Natta.
(4) Different activities of Ziegler catalysts.
(5) Activity and action of modified Ziegler catalysts.

Generally these catalysts are prepared by interaction of an aluminum trialkyl and a transition metal in the form of its halogen derivative. Complex formation between both components is believed to occur according to the tendency of transition elements and aluminum to operate with coordination valences. The catalyst has an extremely high activity (low temperature initiation) and, furthermore, imparts strong protection and stabilization to the growing chain end. This is a prerequisite for the formation of very high molecular weight polymers. Besides the initiation, propagation, and termination, an orientation step is involved in the mechanism of catalysis which produce stereospecific polymers.

In the following section the initiation of olefin polymerization by different kinds of catalysts is discussed in order to show that only one definite type of initiation seems likely to occur under the conditions of the Ziegler polymerization.

INITIATION OF OLEFIN POLYMERIZATION

An olefin could theoretically be activated in three ways; by a radical, a cation, or an anion[3]. In polymerization with Ziegler catalysts, a radical mechanism can hardly explain a stereospecific orientation of α-olefins and the resulting formation of isotactic polymers. The fact that very high molecular weight polyethylene is obtained at very low concentrations of the monomer is even less explicable by a radical polymerization. The propagation would soon be

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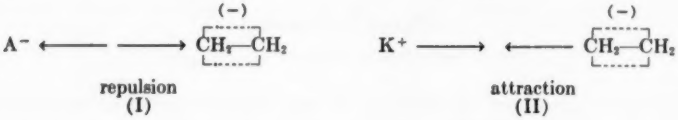
stopped by mutual termination of the chain ends and only polymers of low molecular weight would be formed[4].

An ionic mechanism is favored by most researchers.

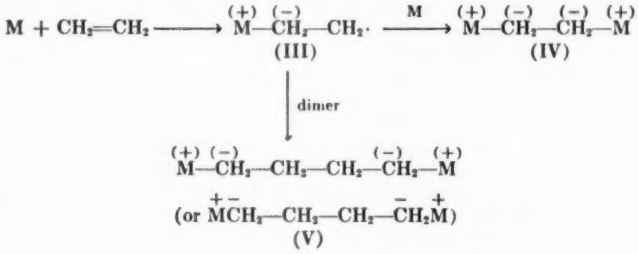
If the initiating agent were an anion, an electrostatic repulsion between the π-electron cloud of ethylene and the anion can be expected to lessen or prevent an approach or absorption of the monomer in the anion sphere (I):



where A^- is an anion and K^+ is a cation.

In a truly anionic initiation the anion would have to add an additional electron to the already existing π-electron pair of the ethylene to create a carbanion. This is energetically unlikely in a system of poor resonance such as ethylene, particularly under moderate conditions. Hence metal alkyls do not initiate ethylene by their carbanion but by their metal cation.

Alkali metals polymerize monomers only when they can form addition products, thus producing a polarized or an ionized metal-carbon bond (M—C bond) on which new monomer units can polymerize. Lithium or sodium does not polymerize ethylene because their reactivity (electro positivity) is not strong enough to produce a M—C bond in the form of the highly reactive and unstable (because resonance-poor) carbanion radical (III) and the corresponding adduct (IV) or dimerization product (V). Only cesium seems to give such products to a certain extent[5].



where M is metal (Cs).

In contrast to ethylene, conjugated dienes or styrene can be polymerized with Li or Na because they can form adducts with enhanced mesomeric possibilities[6]. The activity of the M—C bond formed in this manner is moderate because of higher resonance (allyl anion), and the stability of the carbanion is increased up to a level where terminations occur less frequently and the propagation can be carried on to polymers of higher molecular weight.

When a cation is the initiator (II), attraction would arise between its positive charge and the π-electrons of the monomer. An absorption of the electrons by the cation would create a carbonium ion at the end of the monomer:

The strength of this carbonium ion would depend on how strongly the cation can bind these π-electrons. According to Pauling[7], transition elements offer high resonance to accepted electrons because not only the outer electron shell but also the inner orbitals can participate in resonance stabilization. The great tendency of these elements to form complexes is explained this way. For this reason a cation of a transition metal would have an exceptionally high ability to bind the π-electrons of the monomer and to induce a strong carbonium ion.

It is known that ethylene at low temperatures is attacked by protons and cations which, depending on their counter ions, can form addition products. When strong acids add to the double bond, the π-electrons form a helium doublet with the proton (VI). Certain metal compounds, such as salts of mercury or copper, react the same way yielding very stable M—C bonds even in aqueous medium. In this case the activation of the ethylene would also occur on the cation (VII).

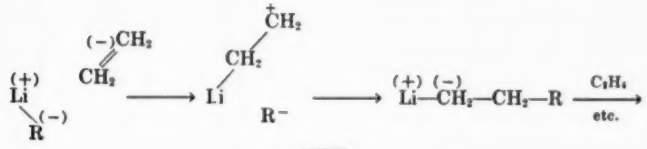
$$H^+CH_2{=}CH_2 \longrightarrow CH_3{-}\overset{+}{C}H_2 \xrightarrow{A^-} CH_3{-}CH_2{-}A$$

(VI)

$$HgCl_2 \xrightarrow{H_2O} \overset{(+)}{ClHg}{-}\overset{(-)}{OH} \xrightarrow{C_2H_4} ClHg{-}CH_2{-}\overset{+}{C}H_2{-}\overset{-}{O}H \longrightarrow ClHg{-}CH_2{-}CH_2{-}OH$$

(VII)

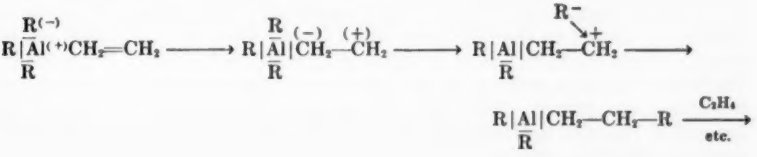
The M—C bond in alkali metal alkyls has a saltlike character[8]. Its reactivity is so strong that it allows ethylene to polymerize to some extent, initiated cationically and propagated anionically. Only short chains are formed because the M—C bond is too reactive. The Li cation tends to terminate the polymerization by H^- extraction in the following example:



(VIII)

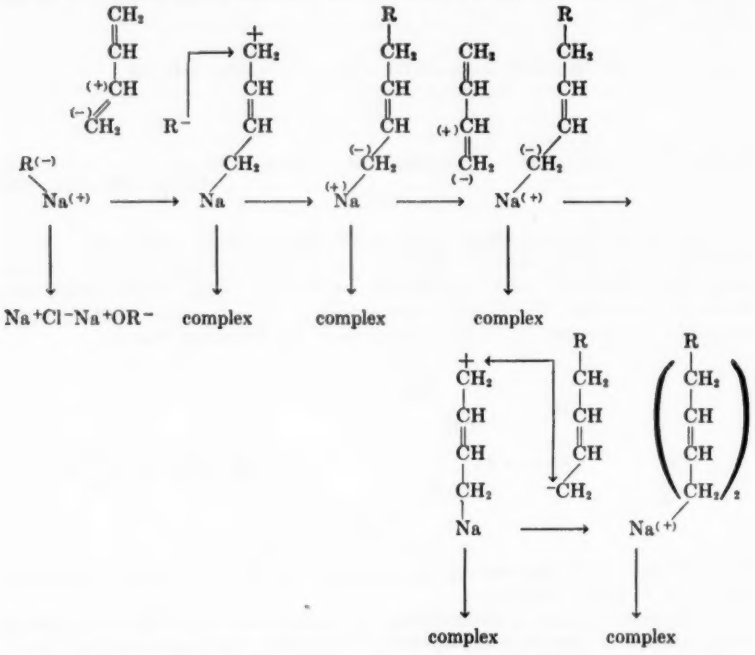
The lifetime of the ions during the migration of the R^- (VIII) is extremely short due to lack of resonance.

In Ziegler's aluminum trialkyl process, characterized by addition of ethylene to an aluminum carbon bond up to low molecular weight polymers or higher olefins, a similar mechanism is involved. Here aluminum has the additional driving force to react with the π-electrons of ethylene with the formation of an electron octet.

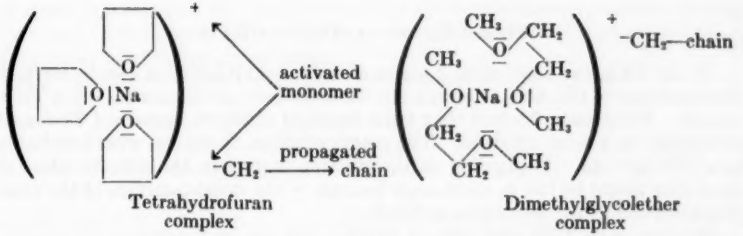


The "living ends" in the diene polymers investigated by Szwarc and coworkers[9] are ionized M—C bonds of higher stability on which further monomers can polymerize. The sodium cation is resonance-stabilized by complex formation with certain ethers and the activity of the M–C bond is decreased to such a degree that only conjugated dienes polymerize.

Another example of a resonance-stabilized M—C bond is the alfin catalyst[10] which contains a sodium alkyl embedded in a highly polar surrounding with extensive mesomeric possibilities (resonance complex or crystal formed with NaO-isopropyl, NaCl). In this case the M—C bond is even more stabilized and the carbonium ion of the activated monomer (butadiene, isoprene) has sufficient lifetime to make rearrangement of the double bond possible. The plus charge appears in the 4-position and effects an almost pure 1,4-polymerization on the solid surface according to the following scheme:



The polymerization of butadiene with sodium is also related to these mechanisms, the sodium forming the real catalyst (M—C bond) by addition and then propagating polymerization mainly in the 1,2-position[11]. The sodium-catalyzed polymerization of styrene in the presence of certain ethers according to Dainton is related to the alfin catalyst and particularly to the Szwarc mechanism as far as the reduction of the activity by complex formation is concerned. The sodium cation is decreased in its activity to a suitable degree by formation of a complex with ethers. The Na^+ can form an electron octet by means of coordination valences to the oxygen atoms of the ether, assuming that the ether molecules can form dipoles.



Tetrahydrofuran complex

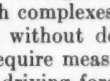
Dimethylglycolether complex

In all the above-mentioned examples an oriented polymerization is not possible simply because there is no fixed location of both cation and anion. The monomer therefore cannot find two fixed poles which are necessary for its orientation. This differs basically from the stereospecific Ziegler-Natta catalysis where initiation and propagation are taking place on two different fixed spots of the catalytic surface within molecular dimensions.

POSSIBLE STRUCTURES OF ZIEGLER CATALYSTS AND THE MECHANISM OF THE POLYMERIZATION

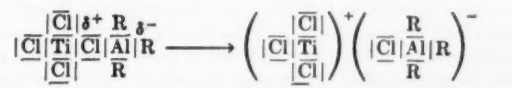
According to the foregoing study, a cation is expected to be the initiator of ionic olefin polymerizations. A transition metal is most likely to supply a reactive cation and at the same time offer enough resonance to enhance the lifetime of the created carbonium ion for the propagation. A fixed location of the cation is required for the orientation. The counter ion, being either the propagation starter (R^- or H^-) or the growing negative chain end, has to have a fixed location, too, to make orientation possible as is discussed below. Anionic propagation and orientation of the monomer can be explained with R^- being the member of an insoluble complex anion.

The tendency of aluminum to form negative complex ions is known. Aluminum trialkyls have a strong driving force to form addition complexes with electron donors. Such complexes with ethers, amines, etc. are so stable that they can be distilled without decomposition, and the removal of the accepted molecule would require measures so strong that the whole molecule would be destroyed. The driving force is mainly to form an electron octet. In the case of aluminum chloride this force is so strong that the compound is still bimolecular at 200° C and only at 800° C is it completely dissociated. The dimer is split by ether, but only to form another electron octet (IX).



(IX)

In the Ziegler catalyst, $TiCl_4/AlR_3$, the aluminum trialkyl has the possibility of forming an electron octet by using one Cl atom of the $TiCl_4$ as an electron donor. The first formed association complex can dissociate, creating a Ti^+ ion and a negative Al complex ion, and thereby making an active spot for polymerization on the catalyst surface.



or:

$$TiCl_4 + AlR_3 \longrightarrow (TiCl_3)^+(AlR_3Cl)^-$$

If the $TiCl_4$ can react with 2 moles of AlR_3, a $(TiCl_2)^{2+}$ ion can be formed. The tendency of the AlR_3 to reduce the Ti apparently predominates when $TiCl_4$ is used. Friedlander[12] found that some modified catalysts contained Ti almost exclusively in a 4-valent state. The reactive cation, therefore, would probably be a $(TiCl_3)^+$ ion. Depending on the starting materials, the concentration of these ions would be low in most cases because of the decomposition of the complex resulting in the reduction to $TiCl_3$.

Starting with $TiCl_3$ and AlR_3, a $(TiCl_2)^+$ ion can be formed:

$$TiCl_3 + AlR_3 = (TiCl_2)^+(AlR_3Cl)^-$$

$TiCl_2$ would give a $(TiCl)^+$ ion:

$$TiCl_2 + AlR_3 = (TiCl)^+(AlR_3Cl)^-$$

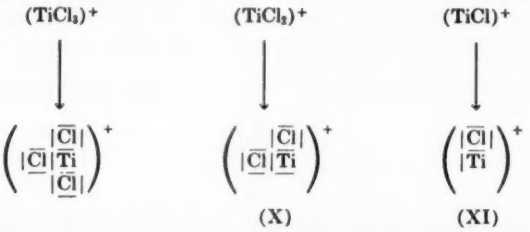
All Ti cations would differ in electron configuration and structure and, for this reason, they would also differ in reactivity. Hence, the affinity for bonding the π-electrons of the monomer (activation) would change with the kind of Ti halide present. The special activity of transition metal cations ought to be explainable by three main characteristics operating jointly:

(1) The positive charge which attracts the π-electrons of the monomer.

(2) The tendency of the cation to accept these electrons in order to neutralize its charge and to fill up its outer orbital again, if possible to an octet.

(3) The additional participation of inner orbitals in resonance stabilization of these electrons.

Different reactivities of Ti cations of equal positive charge in the polymerization of ethylene could be caused by differences in (*2*). It is known that the reactivity of atoms increases when the number of the electrons they have to accept or to donate decreases in order to attain the next higher or lower noble gas configuration. If this principle is applied to the electron configurations of the following Ti cations

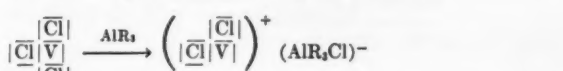


(X) (XI)

$(TiCl_3)^+$ can be expected to be the most reactive (probably too reactive) cation, because it needs only 2 electrons to form the octet. The cations (X) and (XI) would have to accept three or four electrons, respectively, and would be less reactive. The results obtained by comparing the polymerization rates of ethylene with different Ti halides could be explained in this way[13]. A less reactive cation will give a slower polymerization but at the same time causes less side reactions and will yield polymers of higher molecular weight. $TiCl_4$ could give the largest number of different Ti cations with respect to its reduction

by aluminum alkyls. By aging the catalyst all these reactions, complex formations, and reductions would occur slowly, mainly in a semi-solid phase and with continously alternating reactivities.

Vanadium trichloride would give a similar complex formation.

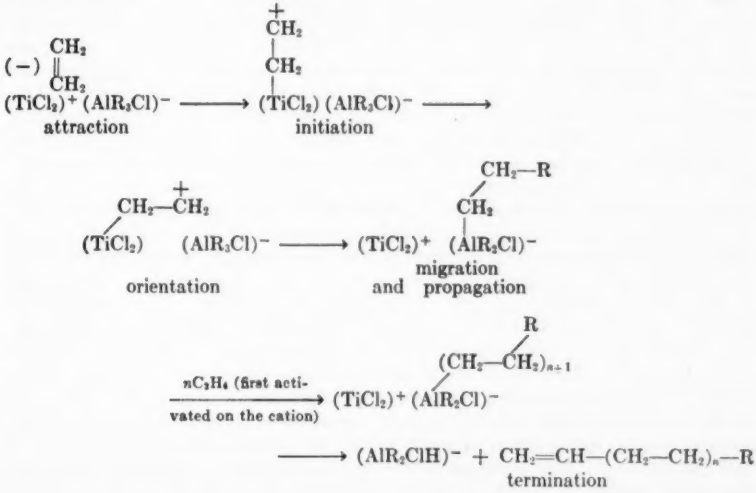


Starting with the $(TiCl_2)^+ (AlR_3Cl)^-$ complex, the polymerization of ethylene would proceed in the following manner. After the monomer is activated on the Ti cation, its positive end orients to the negative complex ion. Now the carbonium ion theoretically has two possible ways to neutralize its charge:

(*1*) The R^- migrates out of the complex and adds to the carbonium ion to form $Cl_2Ti—R$. Since the stability of the negative aluminum complex ion is mostly greater than the stability of the corresponding Ti alkyl ($Cl_3Ti—R$ when $TiCl_4$ is used) there would be no driving force for this reaction. Ti alkyls of this structure tend to decompose[14], particularly in their pre-ionized form, $(TiCl_2)^+R^-$ or $(TiCl_3)^+R^-$, to yield the reduced Ti halide and R radicals which disproportionate. If this decomposition takes place, polymerization would be interrupted because of the destruction of the active ions.

(*2*) Because the complex-stabilized R^- has no tendency to leave its stable state to form a less stable compound, it neutralizes the activated system by pulling the ethylene by its carbonium ion into the negative complex. By this migration of the activated monomer the $(TiCl_2)^+$ ion is reformed and the growing polymer chain is stabilized in the complex ion at the same time. The next monomer again is initiated on the Ti cation and the whole process starts once more. All further monomers add in the same way until a very large chain is formed which undergoes termination by H^- extraction.

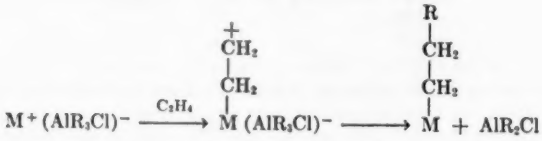
The scheme of ethylene polymerization is shown by the following sequence of reactions:



It can be postulated from this mechanism (as already indicated) that the polymerization would be prevented when the Ti could form a M—C bond with an alkyl group of the aluminum alkyl, because of the destruction of the Ti cation according to the following reactions:

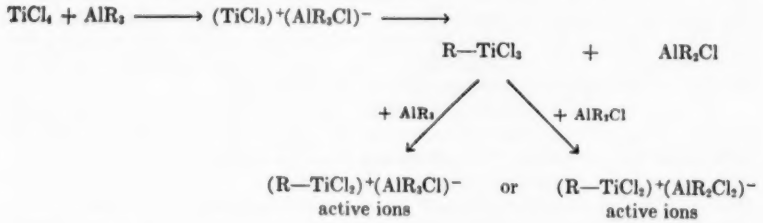
$$M^+(AlR_2Cl)^- \longrightarrow M{-}R + AlR_2Cl$$

or:



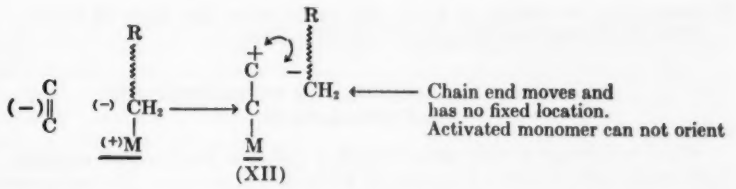
where M is a metal (transition element).

However, when the Ti alkyl is stable enough (low temperature) to react again with Al alkyl, it can form another pair of active ions:



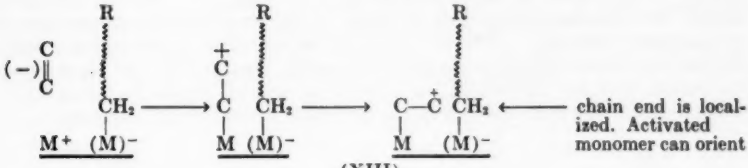
Pd and Pt do not act as catalysts for the polymerization, evidently because of the formation of stable complexes with the monomer[15]. The same is true for mercury and copper, as far as the stability of their M—C bonds is concerned, which has already been mentioned. The growth of one long polyethylene chain from one active spot of the catalyst surface and the orientation is explained by the above-described mechanism, involving two fixed ions. In the case of propylene this yields the isotactic polymer. The active spots are spatially separated complex ions, the negative complex ion supplying the propagation-starter (R^-, H^-). The structure of this complex anion will be different when complex formation takes place with mono- or dialkyl aluminum derivatives or when Ti is the central atom instead of Al. Changes in structures of the anion as well as the cation therefore will influence the polymerization. The sensitive orientation step will be particularly concerned, as will be discussed later in the stereospecific polymerization of propylene.

Comparing the mechanism of Ziegler catalysts with the mechanisms of all other catalysts mentioned in the first part of this treatise, we can conclude that the polymerization in Ziegler's system occurs on two metal atoms. In the case of the other catalysts only one metal atom is involved. The initiation in Ziegler catalysts is performed by a cation of a transition metal and the propagation carried on in a negative complex ion of aluminum or another complex-forming metal. The difference between catalysis on one or two metal atoms becomes especially important in oriented polymerization. If the chain end (or R^-) anchors on one metal atom only, orientation is impossible, because the polymer chain can move away and change its location after the monomer is activated (XII). This is opposed to a two-metal system where the monomer can orient, assuming that both cation and anion are insoluble (XIII).



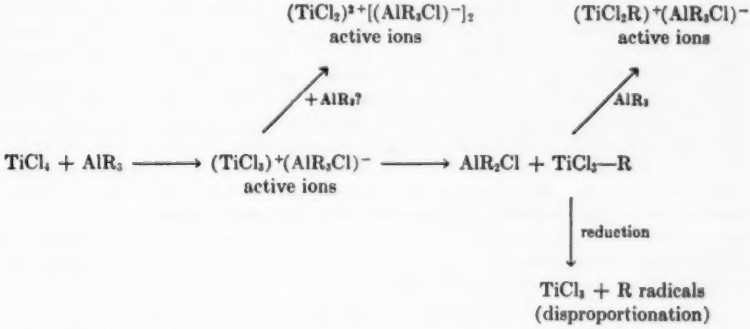
(XII)

where M is a metal, ~ is a polymer chain, and — indicates a solid surface.



(XIII)

The formation of active complex ions would largely depend on the working conditions such as temperature, aging, chemical nature, and ratio of the starting materials. The following possible reactions should be considered in Ziegler catalysts prepared from Ti halides and Al trialkyls.



Whether Ti reacts with one or two moles of AlR_3 to form a *negative* complex ion is questionable. Aluminum cations are expected to be very unstable under these conditions and immediately would react further according to the following scheme:

$$TiCl_4 + AlR_3 \longrightarrow (AlR_2)^+(TiCl_4R)^- \xrightarrow[+\,TiCl_4]{} (TiCl_3)^+(TiCl_4R)^- + AlR_2Cl$$

active ions

The active ions could decompose to yield $TiCl_3$, $TiCl_4$, and R radicals. $TiCl_3$ complexes with AlR_3 to give the ions $(TiCl_2)^+$ $(AlR_3Cl)^-$ mentioned previously. Decomposition of the complex, which can be promoted by higher temperatures, would yield $TiCl_2$:

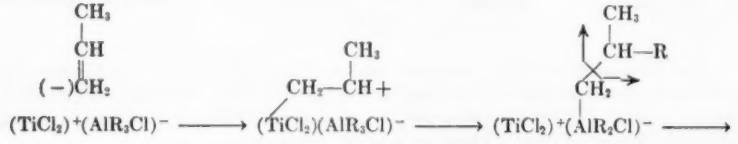
$$\longrightarrow AlR_2Cl + TiCl_3—R \longrightarrow TiCl_2 + R \text{ radicals (disproportionation)}$$

Because of the insolubility of $TiCl_3$, side reactions are less likely to occur.

AlR_2Cl can form new complexes with Ti halides.

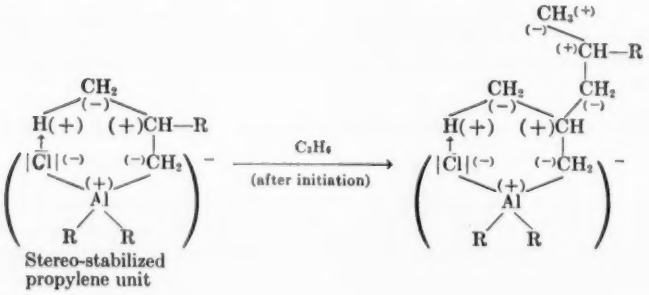
SUGGESTED MECHANISM FOR STEREOSPECIFIC POLYMERIZATION

When propylene is polymerized with a suitable Ziegler-type catalyst, it can form isotactic polymer according to Natta and coworkers. The prerequisite for a constant specific orientation of the monomer is a fixed location of both cation and anion. If either one is soluble or dispersible, atactic polymer will result. With respect to the aforementioned mechanism of ethylene polymerization, the stereospecificity has its origin in the first inter-ion-orientation of the activated monomer. The methyl group of propylene is turned away from the catalyst surface when the prepolarized double bond reacts with the activating cation, and the carbonium ion formed on its end orients to the complex anion. After this first orientation the monomer undergoes propagation:



When the first monomer has migrated into the complex anion, the endgroup outside the complex center could theoretically have free rotation which would destroy the orientation of the methyl group. There must exist one form of stereo-stabilization of the preoriented methyl group. This could be possible by steric hindrance through other members of the complex, but it is more likely that the methyl group forms a hydrogen bond to other substituents of the complex ion, preferably to the most negative one which would be a chlorine atom. Matinet[16] investigated the tendency of methyl groups to form hydrogen bonds with polar groups. According to his experiments, we can expect this hydrogen bond between the methyl group and the chlorine atom which would even be promoted by the formation of a six-membered ring. Internal H bonding of a similar type (between methyl and carboxyl group) has already been suggested by Dippy[17] in the case of *o*-tuluic acid.

Hence the propagation of propylene can be continued in this way:



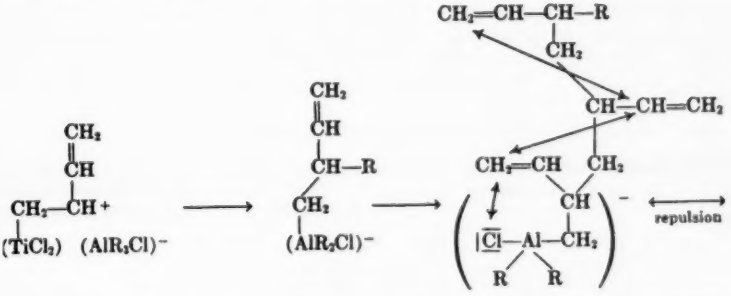
In other words, the methyl group would first be preoriented and directed away from the surface by a "coarse" orientation. After entering the complex anion, this first orientation is corrected toward the chlorine atom and the position of the methyl group stabilized by H bonding. When the next preoriented and activated monomer propagates, its methyl group takes the place on the Cl atom, pushing the first methyl group away. The methyl groups of all further monomers are directed to the same side and will grow continuously on the same polar pattern existing between the complex members in the center of the complex anion.

It could be expected that the methyl group in certain cases could also form H bonds with other chlorine atoms of dissolved Ti halides or with additional chlorine atoms in the complex anion (when $AlRCl_2$ or AlR_2Cl are used). The continuous orientation on one Cl atom could be disturbed in this way, thus decreasing or preventing the formation of isotactic polymer.

According to Matinet's results, a very slight H bonding could even be expected between the methyl groups of isotactic polypropylene. The resulting formation of twisted six-membered rings would impart additional polar symmetry and high internal packing to the polymer chain, thus promoting crystallization and contributing to the regular identity periods of the helically ordered methyl groups.

Styrene could be stereo-stabilized by a polar association between its positively polarized *ortho* C atom and the Cl atom of the complex anion. The alternating polarization in a six-membered ring could give a similar stability as in the case of propylene.

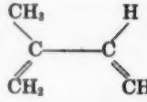
The production of syndiotactic polymer from butadiene could also be explained by the nature of the complex anion with respect to the polarization of the substituents going to be syndio-oriented. When the activated monomer enters the complex anion, the repulsion between the negative complex center and the π-electrons of the vinyl group becomes effective. The vinyl group is pushed away to one side and the vinyl group of the next monomer to the other side, etc. The repulsion between the vinyl groups themselves forces them to go into opposite positions.



The polymerization of conjugated dienes in 1,2 or 1,4-position and the formation of syndiotactic and *cis* or *trans* structures depends on many influences not only of the cation and anion but also of the medium. Ion sizes, their reactivities, and distances to each other could determine 1,2 or 1,4-polymerization. Furthermore, the influence of solubility, H bonding, dielectric properties of the complex members as well as the effect of the surrounding molecules (excess

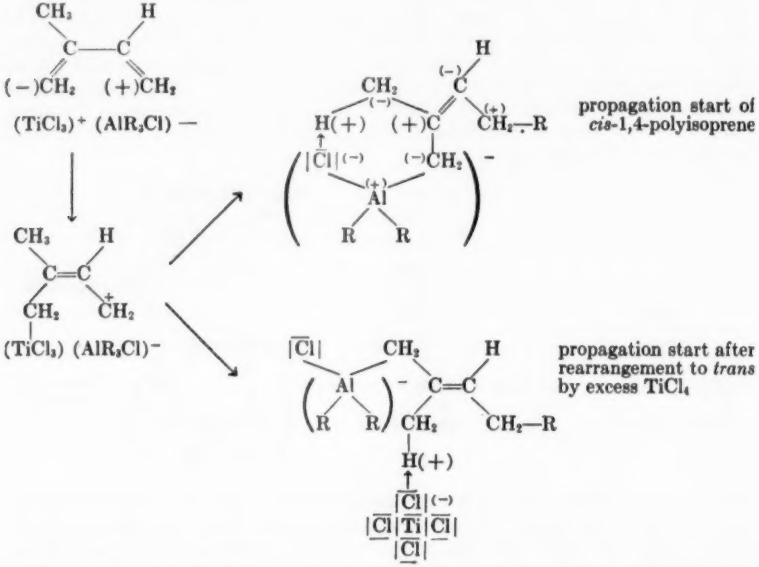
starting materials, by-products) in their ability to divert the activated monomer or catalyzing side reactions has to be considered.

A major factor in the tendency to form *cis* or *trans* polymers is the geometric structure of the conjugated diene. In monomeric isoprene the "*cis*" structure predominates (85 to 90%)[18]



and will yield *cis* polymer if the monomer is not rearranged into *trans* during its excited state. Polar agents, such as by-products in the catalyst formation or excessive starting materials, can attack the methyl group, shifting it (regularly or irregularly) from *cis* to *trans* by temporary H bonding.

cis-1,4-Polyisoprene has been reported to be obtained with $TiCl_4$/Al-trioctyl in a molar ratio of about 1:1[19]. This can be understood by the formation of the complex $(TiCl_3)^+[Al(C_8H_{17})_3Cl)^-$. Due to equivalent amounts of the starting materials, there is no excess $TiCl_4$ which can cause *trans* rearrangement of the activated monomer. The dielectric medium produced by the octyl groups around the negative complex center additionally promotes the undisturbed *cis* polymerization of the isoprene. After migrating into the complex anion, the methyl group moreover can be expected to form a hydrogen bond to the chlorine atom which can provide a certain stabilization of the original *cis* form against diverting agents.



The energy required for the rearrangment into *trans* isomer need not necessarily be supplied by polar impurities in the catalyst system. It can be expected that

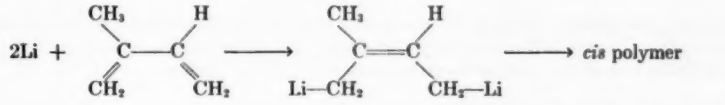
a too high activity of the catalyst itself (the cation mainly) supplies so much energy to the activated monomer that the energy level for the *trans* rearrangement is reached. (See remarks under ref. 19.)

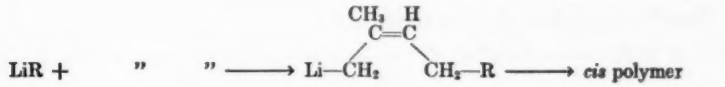
The preparation of *cis*-1,4-polyisoprene from mainly "*cis*" isoprene is not a stereospecific polymerization, which means the creation of a new geometric structure in the polymer. The principal objective is the preservation of the *cis* form of the monomer during its polymerization. Summing up, this seems to be controlled by:

(*1*) The exclusion of polar impurities during polymerization which could catalyze the shift from *cis* to *trans* (soluble halides).

(*2*) The choice of a catalyst whose activation energy is just high enough to catalyze 1,4-polymerization but not so high as to cause *trans* rearrangement.

From this point of view, it seems to be unimportant whether the catalyst is soluble or insoluble. Lithium as an insoluble catalyst[20] or lithium alkyl as a soluble one[21] has been used to produce *cis*-1,4-polyisoprene. Both catalysts meet the requirements (besides the above Ziegler catalyst) for the conservation of the *cis* structure during polymerization. Polar by-products are absent, and both agents form M—C bonds with a moderate energy level on which further monomers can polymerize without being rearranged to *trans*. A complex with Li will stabilize the *cis* form.





Contrary to isoprene, butadiene exists mainly in the "*trans*" form[22] which, in the monomer and in the 1,4-polymer, seems to be its most stable geometric form. Hence the monomer prefers to yield 1,4-*trans* polymer. Its conversion into *cis* polymer is a real stereospecific polymerization[23].

MODIFIED ZIEGLER CATALYSTS

These catalysts must also meet the requirements postulated in the foregoing sections: the formation of a cation of a transition element and a negative complex with a propagation-starter such as R^- or H^-.

LITHIUM ALKYL $TiCl_4$

Ti cations can be formed in different ways as shown below. Lithium (contrary to Al) reaches the next *lower* octet by giving away one electron to form a lithium cation. That is the reason the lithium alkyl tends to complex with $TiCl_4$:

$$Li^+(TiCl_4R)^- \xrightarrow{\text{excess LiR}} (Li^+)_2(TiCl_4R_2)^{2-}$$

The Li^+ can react further with excess $TiCl_4$ to form LiCl and a Ti cation. By extraction of an alkyl group from the complex, reduction to Ti^{III} occurs. The $TiCl_3$ again can complex with Li alkyl and the Li cation can be substituted by another Ti cation according to the following scheme:

$$Li^+(TiCl_4R)^- \longrightarrow LiCl + TiCl_3R \longrightarrow TiCl_3 + \text{R radicals (disproportionation)} \quad (1)$$

$$\downarrow + TiCl_4$$

$$\underset{\text{active ions}}{(TiCl_3)^+(TiCl_4R)^-} + LiCl \longrightarrow TiCl_4 + TiCl_3 + \text{R-radicals}$$

$$LiR + TiCl_3 \longrightarrow Li^+(TiCl_3R)^- \longrightarrow LiCl + TiCl_2R \longrightarrow TiCl_2$$

$$\downarrow + TiCl_3 \text{ (or } TiCl_4)$$

$$\underset{\text{active ions}}{(TiCl_3)^+(TiCl_3R)^- + LiCl \quad [\text{or } (TiCl_3)^+(TiCl_3R)^-]}$$

If $TiCl_2$ is formed, further reactions are possible in the aging process of the catalyst. Excess LiR can prevent the formation of Ti cations; therefore sufficient $TiCl_4$ has to be present to substitute the lithium cations.

SODIUM HYDRIDE $TiCl_4$

Possible ways of catalyst formation are:

$$TiCl_4 + NaH \longrightarrow Na^+(TiCl_4H)^- \longrightarrow NaCl + TiCl_3H \longrightarrow TiCl_3 + {}^1/_2H_2$$

$$\downarrow + TiCl_4$$

$$\underset{\text{active ions}}{(TiCl_3)^+(TiCl_4H)^-} + NaCl \longrightarrow TiCl_3$$

Whether Ti reaches its coordination number 6 by adding two moles of NaH is questionable.

$$TiCl_3 + NaH \longrightarrow Na^+(TiCl_3H)^- \longrightarrow NaCl + TiCl_2 + {}^1/_2H_2$$

$$\downarrow + TiCl_3 \text{ (or } TiCl_4)$$

$$\underset{\text{active ions}}{(TiCl_3)^+(TiCl_3H)^-} \longrightarrow TiCl_2$$

$LiAlH_4/TiCl_4$ CATALYST

$$TiCl_4 + LiAlH_4 \text{ (or } LiAlR_4) \longrightarrow (TiCl_3)^+(AlH_4)^- + LiCl$$

Reduction can occur by decomposition of the complex to $TiCl_3$, AlH_3, and $\frac{1}{2}H_2 \cdot TiCl_4$ or $TiCl_3$ can react again with AlH_3 with formation of $(TiCl_3)^+(AlH_3Cl)^-$ or $(TiCl_2)^+(AlH_3Cl)^-$. The latter can decompose to $TiCl_2$, AlH_2Cl, and $\frac{1}{2}H_2$ which can react further.

CATALYSTS OF MOLYBDENUM, CHROMIUM, NICKEL, COBALT, ETC. ON CARRIERS

The mechanism apparently is related to the above-described Ziegler catalysis. The necessity of carriers like alumina points out that this material plays an important role in the catalysis. It probably forms the negative complex ion in which a propagation starter, such as H^-, is introduced by a promoting agent (H_2, hydrides). Hydride formation on the carrier metal yields metal alkyl by monomer addition. The transition metal supplies the active cation for the initiation which can be present in different valence states. Active complex ions similar to these (but without propagation starter) are probably the active spots in dehydration catalysts prepared from compounds of transition metals and alumina.

TABLE I

SCHEME FOR SOME POLYMERIZATIONS OF OLEFINS ON METAL-CARBON BONDS

Starting material for catalyst	Active catalyst (metal-carbon bond)	Typical monomer	Initiation	Propagation
Li, R—Cl	$Li^{(+)}—R^{(-)}$	Isoprene	Cationic	Anionic
Al, H_2, olefin	$R_2Al^{(+)}—R^{(-)}$	Ethylene	Cationic	Anionic
Na, butadiene	$\overset{(+)}{Na}—CH_2—$monomer rest[a]	Butadiene	Cationic	Anionic
Na, ethylene	No catalyst (no metal-carbon bond formed)			
Cs, ethylene	$\overset{(+)}{Cs}—CH_2—CH_2—\overset{(-)}{Cs}$	Ethylene	Cationic	Anionic
	$\overset{(+)}{Cs}—CH_2—(CH_2)_2—CH_2—\overset{(-)}{Cs}$			
	Alfin catalyst			
Na, R—Cl, isopropanol	$\overset{(+)}{Na}—R$ ↓ complex	Butadiene Isoprene	Cationic	Anionic
Na, ethers, monomer	$\overset{(+)}{Na}—CH_2—$monomer-rest ↓ ether complex	Butadiene Styrene	Cationic	Anionic
Na, ethers, naphthalene, monomer	$(Na^+)_2(\text{naphthalene})_2^-$ ↓ 2-butadiene	Butadiene	Cationic	Anionic
	$^-CH_2—CH(CH=CH_2)—CH(CH=CH_2)—CH_2^-$			
$TiCl_2$, AlR_3	$(TiCl_2)^+(AlR_2Cl)^-$	Ethylene	Cationic	Anionic
HBr, $AlBr_3$, monomer	$R_2\overset{+}{C}H(AlBr_4)^-$	Propylene α-olefins	Cationic	Cationic

[a] Can be the 1,4-adduct or a dimer.

ADDENDA

After this article had been submitted for publication, the following data were found which support the suggested mechanisms.

(*1*) Based on the mechanisms discussed in this treatise the exact structure and the active form of the complex $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$ obtained by Natta and co-workers (*Angew. Chem.* **69**, 686) from $Al(C_2H_5)_3$ and titanium dicyclopentadienyl dichloride can be explained by the following sequence of reactions:

$$(C_5H_5)_2TiCl_2 + Al(C_2H_5)_3 \longrightarrow (C_5H_5)_2TiCl^+[Al(C_2H_5)_3Cl]^-$$

$$\longrightarrow (C_5H_5)_2Ti\begin{matrix}Cl\\ \diagup\\ \diagdown\\ C_2H_5\end{matrix} + Al(C_2H_5)_2Cl$$

$$\downarrow$$

$$(C_5H_5)_2TiCl + \cdot C_2H_5 \xrightarrow[\text{tionation}]{\text{dispropor-}} {}^1/_2C_2H_4 + {}^1/_2C_2H_6$$

$$\downarrow + Al(C_2H_5)_2Cl$$

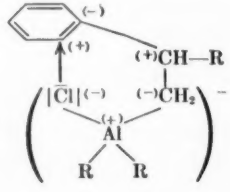
$$(C_5H_5)_2Ti^+\ [Al(C_2H_5)_2Cl_2]^-$$
active ions

The Ti^{III} cation initiates ethylene and the propagation occurs in the aluminum complex anion.

The formation of the corresponding complexes from $AlCl_2C_2H_5$ and $AlCl(C_2H_5)_2$ would be similar and the following structures would result:

$$(C_5H_5)_2Ti^+(AlCl_3C_2H_5)^- \quad \text{and} \quad (C_5H_5)_2Ti^+(AlCl_4)^-$$

(*2*) The stereostabilization of styrene in a negative complex ion of Al can be explained by an association between the negative chlorine atom and the positivated *ortho* position of the benzene ring. The six-membered ring formed is stabilized by alternating polarization. This postulated association is supported by Allred and Rochow [*J. Am. Chem. Soc.* **79**, 5361 (1957)] who found that even benzene associated with alkylchlorides in such a manner that the chlorine atom is *oriented perpendicular* to the plane of the benzene ring. The same would be true for the styrene-aluminum complex. This kind of orientation can be expected to be much stronger with styrene in a negative, chlorine containing complex because of a stronger polarization.



(4) It was postulated in this treatise that titanium can form both a cation and a negative complex ion. Recently a titanium alkyl compound (CH_3TiCl_3) has been patented by Farbwerke Hoechst, Germany, for the polymerization of ethylene. This catalyst works only above 60° C. It can be expected that above this temperature complex formation and reduction occur, for instance

$$CH_3TiCl_3 \xrightarrow{60°\ C} TiCl_3 + CH_3\cdot\ (\longrightarrow \text{side reactions})$$
$$TiCl_3 + CH_3TiCl_3 \longrightarrow (TiCl_2)^+(TiCl_4CH_3)^-$$
$$\text{or } (TiCl_3)^+(TiCl_3CH_2)^-$$

In this case complexes are formed with III- and IV-valent Ti which can be expected to have catalytic activity. Complexes with only IV-valent Ti could be formed, too, such as $(CH_3TiCl_2)^+(TiCl_4CH_3)^-$ etc. Whether they have catalytic activity cannot be decided yet.

SYNPOSIS

The polymerization of olefins with Ziegler catalysts is an intercomplex ion polymerization taking place on two metal atoms. A cationic initiation occurs on a cation of a transition element. In the case of a stereospecific polymerization the activated monomer orients toward and inside a negative complex ion (for instance of aluminum) into which it migrates by adding a propagation starter (R^-, H^-). In this complex anion all further cationically activated monomers propagate anionically until termination occurs by H^- abstraction.

REFERENCES

[1] Only a few publications and patents concerning Ziegler catalysis are cited in this paper. Complete literature of the important work done in this field by K. Ziegler, G. Natta, H. Mark, and many other researchers can be found in the publications of the above-mentioned authors.
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[3] A weak polar bond would not be efficient enough to cause a strong polarization of the ethylene and start polymerization at room temperature.
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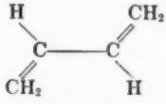


"*trans*" butadiene

[23] G. Natta, *Chimica e industria Milan* **39**, 653 (1957). The formation of *trans*-1,4-polybutadiene is stereo-preserving. The polymerization to *cis*-1,4-polybutadiene is stereospecific. R. A. Stewart et al. [*Ind. Eng. Chem.* **45**, 173 (1953)] obtained *trans*-1,4-polybutadiene with alfin catalysts. This polymerization is also stereo-preserving.

POLYBUTADIENES OF CONTROLLED *CIS*, *TRANS* AND VINYL STRUCTURES *

J. N. Short, G. Kraus, R. P. Zelinski, and F. E. Naylor

Phillips Petroleum Company, Bartlesville, Oklahoma

INTRODUCTION

There are four ways in which butadiene molecules may link up in polymerization to produce linear macromolecules of perfect order. If the polymerization proceeds by 1,4 addition, the internal double bonds of the polymer chain may all have the *cis* or the *trans* configuration. If the polymerization takes place by 1,2 addition with the butadiene units linked head-to-tail, two different types of orderly structures are possible, depending on whether the asymmetric carbon atoms in the chain assume the same configuration either all *d* or all *l*, or whether they alternate in regular fashion between the *d* and *l* forms. The first of these arrangements has been termed "isotactic", the second "syndiotactic". In either case the double bond is present in a vinyl branch. The four forms of ordered polybutadienes are shown in Figure 1. Because of the regularity of the chains, polybutadienes approaching 100 per cent of any one of these structures will be crystallizable polymers. If, however, the elements of two or more of these structures are combined randomly along the polymer chain, amorphous polymers of entirely different properties result. For example, "atactic" vinyl polybutadiene, in which the *d* and *l* units combine randomly, differs somewhat from the other "mixed" polymers in that its double bond composition is still homogeneous—all vinyl. A somewhat similar amorphouse vinyl polybutadiene would arise from random head-to-tail and tail-to-tail arrangement. All other "mixed" polybutadienes involve distribution of the unsaturation over the *cis*, *trans* and vinyl configurations.

In a previous paper from these laboratories the properties of 1,4-polybutadiene were described as a function of *cis*:*trans* ratio[1]. The present report deals with an extension of this work to cover the configuration spectrum more completely and has been made possible through the development of stereospecific catalyst systems capable of tailoring polybutadiene to almost any desired configuration. Particular emphasis will be placed on the technologically most promising areas of configuration.

STRUCTURE AND PHYSICAL PROPERTIES

Although it is difficult to obtain polymers of completely regular structure, the pure forms have been approached so closely that there can be no doubt as to their crystalline nature. Below their melting points these polymers are strong, crystalline plastics; above their melting points they are rubbers (Figure 2). With the exception of *cis*-polybutadiene, the melting points of the various

* An original publication. Presented before the 15th Annual Technical Conference of the Society of Plastics Engineers, New York, N. Y., January 27–30, 1959.

structurally pure forms of polybutadiene lie well above room temperature. However, as monomer units of different configuration are introduced into the chain, the melting points of the polymers drop rapidly, and by far the largest area on the *cis-trans*-vinyl composition diagram is occupied by polymers which are true elastomers at ordinary temperatures. This applies particularly to the crosslinked rubbers (vulcanizates), because crosslinking has the effect of further depressing the melting point.

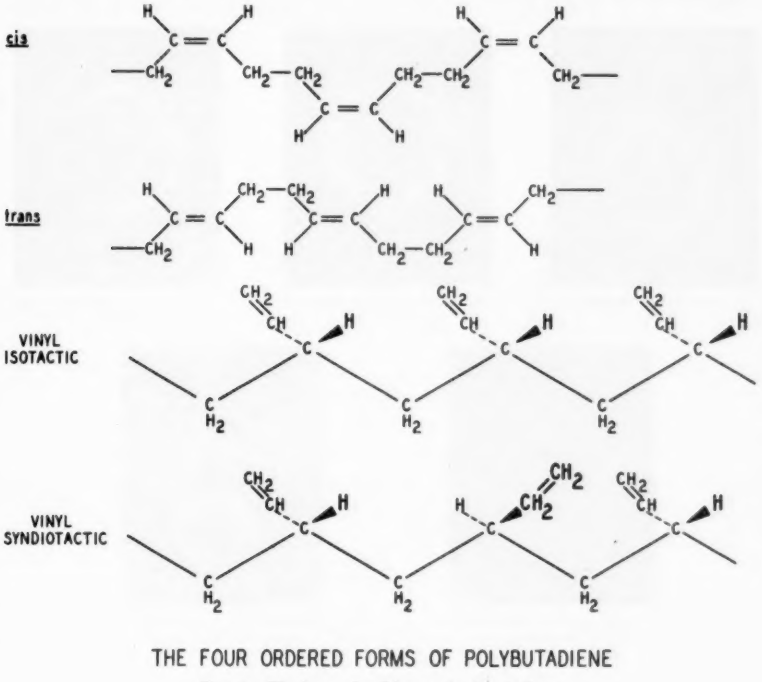
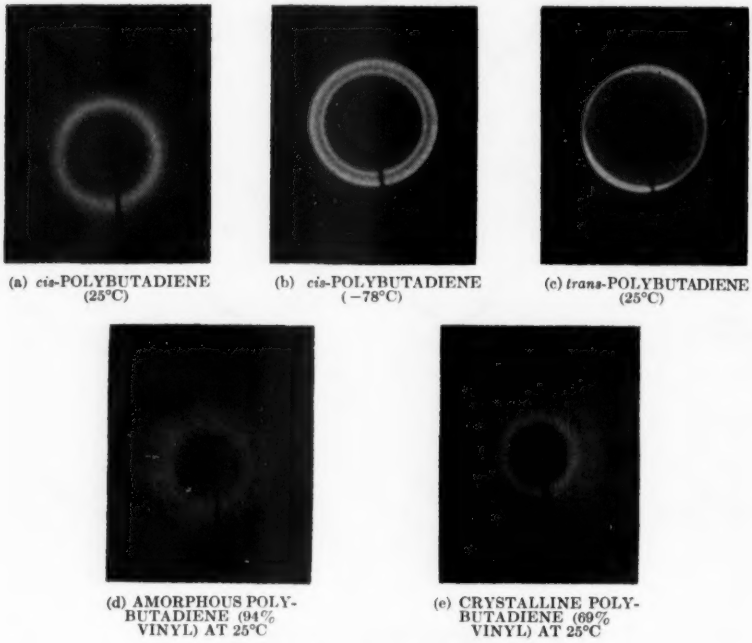


FIG. 1.—The four ordered forms of polybutadiene.

Figures 3 to 8 show the variation of a number of physical properties with configuration. These diagrams were prepared from data obtained in the manner described in our earlier publication[1]. They are based on polymers of approximately equal plasticity, vulcanized to equal states of cure in a simple compounding recipe. Their configurations are listed in Table I. It should be realized that whenever a property changes rapidly in approaching 100 per cent of any one structure, the corner of the diagram will be subject to some doubt because of the necessity for extrapolation. This is especially true of the diagrams representing tensile strength. Figure 3, which shows the tensile strength (at 25° C) of gum vulcanizates, has a flat plateau extending over most of the configuration range, rising sharply toward the *cis* and *trans* corners. Only a moderate rise is shown for the vinyl corner, the polybutadienes represented by the surface being the amorphous, atactic polymers. Isotactic and syndiotactic

vinyl polybutadienes would be represented by different, higher level surfaces, which presumably would merge into the diagram shown at *cis* and *trans* contents high enough to destroy the crystallinity. There are as yet insufficient data available to locate these surfaces accurately, but a number of crystalline high-vinyl polybutadienes have been prepared.

The x-ray diffraction pattern of one such polymer is shown in Figure 2e. The spacing of the rings agrees with the crystallographic data given by Natta[2] for syndiotactic polybutadiene. The x-ray patterns of Figure 2 also show the



(a) *cis*-POLYBUTADIENE (25°C)

(b) *cis*-POLYBUTADIENE (−78°C)

(c) *trans*-POLYBUTADIENE (25°C)

(d) AMORPHOUS POLYBUTADIENE (94% VINYL) AT 25°C

(e) CRYSTALLINE POLYBUTADIENE (69% VINYL) AT 25°C

FIG. 2.—X-ray diffraction patterns of various polybutadienes.

high-*trans*-polybutadiene to be crystalline at room temperature. Polybutadiene of 95 per cent *cis*-configuration is amorphous under these conditions, but crystallizes readily at sub-freezing temperatures.

It is evident that crystallization is necessary for the development of high tensile strength in non-reinforced gum vulcanizates. In the absence of crystallization, increased chain regularity also leads to an increase in tensile strength as the "pure" structures are approached, but the effect is considerably smaller. It is interesting that the type of stretch-induced crystallization responsible for the high gum tensile strength of *cis*-polyisoprene does not appear to be a major factor in *cis*-polybutadienes up to 95 per cent *cis*-configuration. This is indicated by the relatively modest rise in tensile strength with *cis* content and has been confirmed by x-ray data on the stretched rubbers.

Another factor of great importance in determining physical properties is the

glass transition temperature. Figure 4 shows the brittle temperatures of polybutadiene gum vulcanizates as determined by a modified Gehman torsional stiffness test. The modification consisted of quenching the samples from above their melting points to −195° C to avoid crystallization during cooling. This allows the glass transition to be observed even in crystallizable rubbers. Figure 4 shows an extremely low, glass-transition temperature for the predominantly *cis*-polybutadienes. The transition temperature rises gradually toward the high-*trans* region and more abruptly toward the vinyl corner of the diagram.

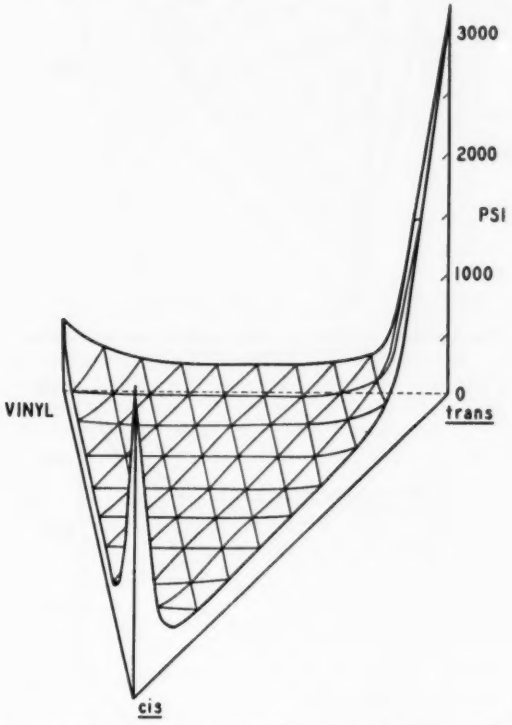


FIG. 3.—Tensile strength of polybutadiene gum vulcanizates at 25° C.

The low glass transition of the high-*cis*-polybutadienes is of great potential importance, for it is only necessary to suppress crystallization through control of structure and/or compounding to make possible the preparation of vulcanizates which remain flexible at very low temperatures. This is discussed in more detail in a later section of this paper. Conversely, the relatively high glass transition temperature of the vinyl polybutadienes may seriously limit their usefulness as elastomers at low temperatures even if crystallization could be suppressed entirely.

From a practical standpoint the properties of carbon black reinforced vulcanizates are of prime importance. Figure 5 shows the tensile strength of

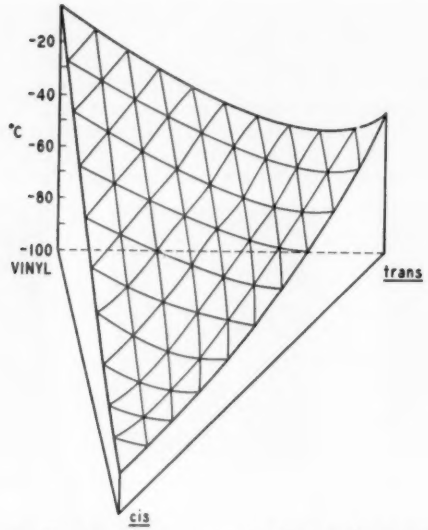


FIG. 4.—Glass transition temperatures as determined by a modified Gehman torsional stiffness test.

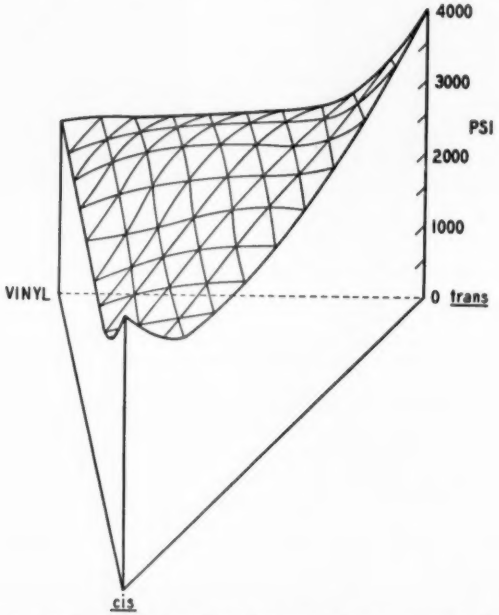


FIG. 5.—Tensile strength of polybutadiene tread type vulcanizates at 25° C.

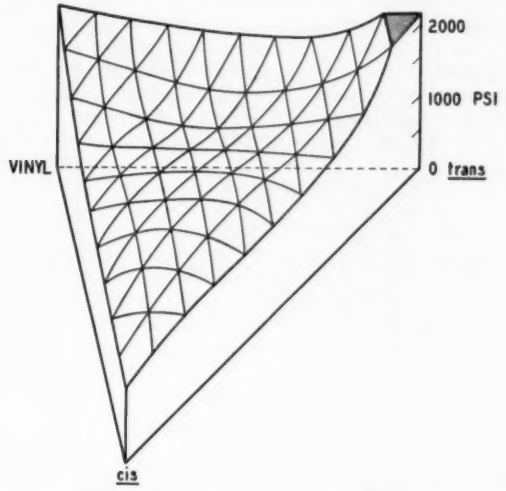


FIG. 6.—Per cent modulus of polybutadiene tread stocks at 25° C. The extreme *trans* corner of the diagram is not defined because samples do not reach 300% elongation before breaking.

polybutadienes reinforced with 50 parts of high abrasion furnace black (Philblack* 0). It will be noted that the plateau has been raised by about 2500 psi as a consequence of carbon black reinforcement. Again, as in the case of gum vulcanizates, the tensile strength rises toward the corners.

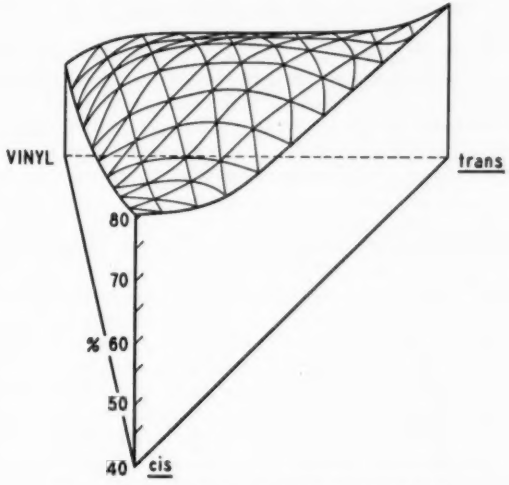


FIG. 7.—Yerzley resilience of polybutadiene tread stocks.

* A trademark.

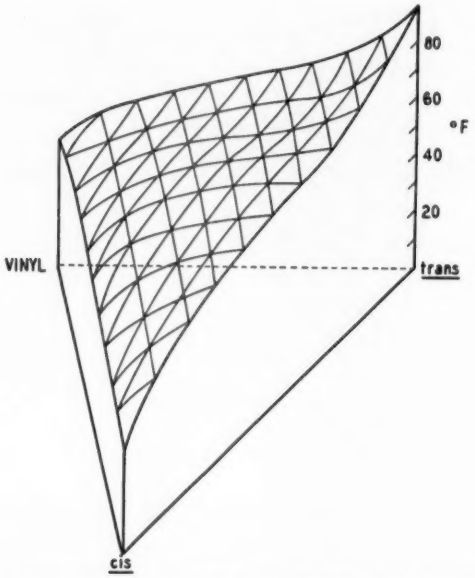


FIG. 8.—Heat build-up of tread stocks determined by Goodrich flexometer test.

The 300 per cent modulus of black vulcanizates (Figure 6) is characteristically low for *cis*-polybutadiene and increases with vinyl and *trans* content. As expected, it is particularly high for the polymers which are crystalline at the test temperature.

Figures 7 and 8 illustrate two dynamic properties—resilience and heat build-up. In the high-*cis* region resilience is high and heat build-up is low, so that the dynamic properties of *cis*-polybutadiene are fully comparable to those of natural or synthetic *cis*-polyisoprenes. The vinyl polybutadienes are characterized by fair dynamic properties. At low temperatures resilience depends on whether the polymer is rubbery, crystalline or glassy. In general, high

TABLE I

CONFIGURATIONS[a] OF POLYBUTADIENES USED IN CONSTRUCTION OF FIGURES 3–8

cis	*trans*	Vinyl	*cis*	*trans*	Vinyl
95.5	0.9	3.6	16.6	80.5	2.9
94.3	1.4	4.3	12.8	30.1	57.1
90.2	4.5	4.3	8.7	10.2	81.1
86.7	8.8	4.5	7.9	74.2	17.9
71.0	27.4	1.6	5.2	5.2	89.6
37.0	52.0	11.0	5.1	9.4	85.5
25.4	43.0	31.6	4.9	26.2	68.9[b]
24.8	72.2	3.0	4.8	93.0	2.2
24.1	0.3	75.6	3.0	3.0	94.0

[a] Configurations were determined by infrared analysis according to the method of Silas, Yates and Thornton, *Anal. Chem.*, in press.
[b] Syndiotactic by X-ray diffraction.

steel-like resilience is observed in frozen crystalline rubbers, whereas, it is lacking in glassy polymers. While the excellent resilience of very highly crystalline polybutadienes is not of the type which would be useful in an elastomer, the inherent resilience of the crystalline phase appears to be responsible for the fact that partial crystallinity does not detract seriously from the resilience of a rubbery polymer. Thus, for instance, *cis*-polybutadiene exhibits excellent resilience over a very wide temperature range, even where crystallization becomes pronounced[1].

CIS-POLYBUTADIENE

In an age of synthetic polymers, natural rubber has retained a dominant position in the manufacture of certain rubber products, particularly in the construction of heavy duty truck tires. In this service it cannot be replaced by ordinary synthetic rubbers without serious sacrifice of performance. Until the advent of ordered polymerization, no synthetic substitute was available to provide a stable, independent supply in quantity sufficient to meet the predicted needs of the future.

TABLE II

COMPOUNDING RECIPE

	cis-Polybutadiene	1:1 Blend of *cis*-Polybutadiene and natural rubber	Natural rubber	SBR 1500
Polymer	100	100	100	100
Philblack O[b]	50	50	50	50
Zinc oxide	3	3	4	3
Stearic acid	2	3	3	1
Antioxidant	1	1	1	1
Resin 731D[a]	3	5	—	—
Philrich 5[b]	5	5	5	10
Sulfur	1.75	2.0	2.0	1.75
NOBS Special[c]	—	0.8	—	—
Santocure[d]	0.8	—	0.5	1.1

[a] Modified wood resin produced by catalytic disproportionation, Hercules Powder Company.
[b] A trademark.
[c] N-Oxydiethylenebenzothiazole-2-sulfenamide, American Cyanamid Company.
[d] N-Cyclohexylbenzothiazol-2-sulfenamide, Monsanto Chemical Company.

The characteristic properties of natural rubber which are believed to be mainly responsible for its performance in truck tires are its superior hysteresis properties of low heat build-up and high resilience which have been ascribed to its regular conformation as an almost entirely *cis*-polyisoprene. These have largely been duplicated in several successful syntheses of *cis*-polyisoprene (synthetic natural rubber)[3]. This same combination of low heat build-up and high resilience is found in *cis*-polybutadiene. This elastomer is of particular interest because it is made from the abundant supply of polymerization grade butadiene which need only be dried before use.

From Figures 3 to 8 it is evident that as the amount of *cis* unsaturation in 1,4-polybutadiene is increased from about 70 per cent of the total to 95 per cent, there is an improvement in those properties of greatest importance. It is particularly apparent close to the maximum *cis* content. When this is 95 per cent of the total unsaturation, unplasticized vulcanizates reinforced with high abrasion furnace black have properties similar to those of natural rubber. Heat buildup of *cis*-polybutadiene (hereafter identifying a polymer with about 95 per cent of this configuration) is equivalent and resilience is higher, especially

at low temperatures. Original tensile properties are inferior to those of natural rubber but adequate, but this is compensated by greater retention of these properties after aging.

For service applications, it is convenient to plasticize *cis*-polybutadiene to improve its processability. Also, for application in tire treads it is desirable to sacrifice tensile strength for improved dynamic properties and abrasion resistance. Table II shows a practical *cis*-polybutadiene tread formulation. Table III summarizes the properties obtained for *cis*-polybutadiene cured in this recipe, and for vulcanizates of natural rubber and SBR 1500.

It is evident that *cis*-polybutadiene is essentially equivalent to natural rubber in its dynamic properties. Of particular interest are the properties of oven aged specimens. *cis*-Polybutadiene not only retains its advantage in resilience; it gains in heat build-up and shows excellent retention of tensile strength.

TABLE III

PROPERTIES OF BLACK-REINFORCED VULCANIZATES

	cis-Polybutadiene	1:1 Blend of *cis*-polybutadiene and natural rubber	Natural rubber	SBR 1500
		Original		
Compression set, %	17	14	14	22
300% modulus, psi	1200	1700	1930	1170
Tensile strength, psi	2600	3350	3840	3490
Ultimate elongation, %	470	520	520	640
Heat buildup, ° F	41	38	41	68
Resilience, %	78	75	70	61
Shore A hardness	60	61	62	58
		Oven aged 24 hours at 212° F		
300% modulus, psi	1850	2210	2340	2330
Tensile strength, psi	2330	2600	2900	3550
Ultimate elongation, %	350	350	390	495
Heat buildup, ° F	34	37	40	53
Resilience, %	82	77	73	67
Shore A hardness	—	67	66	64

Comparison of these results with the properties of vulcanized SBR 1500 (cold rubber) clearly demonstrates the great importance of heat build-up and resilience. For in spite of its excellent tensile strength, cold rubber is not satisfactory for use in truck tires.

As the molecular weight of *cis*-polybutadiene is increased, processing difficulties are encountered because of a sudden decrease in cohesiveness which occurs as the rubber is warmed to about 110° F. However, no serious difficulty arises when *cis*-polybutadiene is blended in a 1:1 ratio with natural rubber. The products can be processed readily in standard factory equipment without special handling and retain the desirable features of each homopolymer[4].

These blends can be cured in a conventional recipe (Table II) to vulcanizates which have excellent hysteresis properties as shown by the low heat build-up and high resilience values of Table III. Furthermore, since most of the characteristic high tensile strength of natural rubber is retained, the blend has the general properties of natural rubber.

Service performance of tire treads made of *cis*-polybutadiene or its 1:1 blend with natural rubber has shown that this polymer has outstanding resistance to

road wear (Table IV). In half-and-half 7:60 × 15 retread tires *cis*-polybutadiene wears 35–40 per cent less than natural rubber or even SBR 1500. This superiority is also evident in the performance of the 1:1 blends where 13–24 per cent improvements in tread rating are noted. In fact, in these passenger tires 1:3 blends of *cis*-polybutadiene and natural rubber are almost the equivalent of cold rubber.

TABLE IV

cis–POLYBUTADIENE COMPOUNDS IN RETREAD PASSENGER TIRES

Experimental tire	Control	No. of tires	Average mileage	Treadwear rating (control =100)
cis-Polybutadiene	Natural rubber	3	7,000	140
cis-Polybutadiene	SBR 1500*	4	12,500	135
50/50 *cis*-polybutadiene-natural rubber blend	Natural rubber	4	10,000	124
50/50 *cis*-polybutadiene-natural rubber blend	SBR 1500	2	9,000	113
25/75 *cis*-polybutadiene-natural rubber blend	SBR 1500	2	9,000	98

* Emulsion styrene-butadiene copolymer.

The 1:1 blend of *cis*-polybutadiene and natural rubber has also been compared with natural rubber in 10:00 × 20 factory-made truck tires (Table V). In either half-and-half or whole tread constructions the blends have been slightly superior in wear resistance and have developed somewhat lower running temperatures than the natural rubber controls. There may exist a slight inferiority in resistance to cracking. Tests are continuing but it is already evident that *cis*-polybutadiene can contribute greatly to the rubber industry's independence of natural rubber.

TABLE V

PERFORMANCE OF 1:1 BLENDS OF *cis*–POLYBUTADIENE AND NATURAL RUBBER IN 10:00 × 20 TRUCK TIRE TREADS

Tread construction	Control	No. of tires	Average mileage	Treadwaer rating (control =100)
Half-and-half	Natural rubber	2	18,750	102
Whole	Natural rubber	2	15,300	102

The strong tendency of high-*cis*-polybutadiene to crystallize at low temperature can be eliminated by reducing *cis* content. When *cis* configuration is lowered to about 80 per cent, polybutadiene vulcanizates have been found to display outstanding freeze resistance. A low-Mooney polybutadiene containing 79 per cent *cis*, 17 per cent *trans*, and 5 per cent vinyl configuration has been studied in detail[5]. This polymer exhibited a brittle point of −97° C (SBR 1500, −52° C; natural rubber, −61° C) and less tendency to crystallize than either natural rubber, cold rubber, or emulsion polybutadiene. The data in Table VI show 80 per cent *cis*-polybutadiene tread stocks to be similar to emulsion polybutadiene in stress-strain properties and to natural rubber in dynamic properties. Gehman freeze point data for these same polymers are presented in Figure 9. Although not now commercially available, this polymer should

TABLE VI

PHYSICAL PROPERTIES OF 80 PER CENT *cis*–POLYBUTADIENE TREAD STOCK

	80% *cis*-polybutadiene	Emulsion polybutadiene	SBR 1500	Natural rubber
Tensile strength, psi	2020	2550	3080	3075
Ultimate elongation, %	380	345	495	450
Shore A hardness	67	65	64	64
Resilience, %	73	64	63	70
Heat buildup, ° F	44	55	53	42
Gehman freeze point[a], ° C	−97	−75	−61	−52

[a] Standard test procedure, ASTM No. D-1053-52T.

be outstanding in arctic rubber applications not requiring high solvent resistance.

TRANS-POLYBUTADIENE

Unlike *cis*-polybutadiene, which is a soft rubbery material, pure *trans*-polybutadiene is a hard crystalline plastic. When molded at a temperature somewhat higher than its melting point (ca. 150° C), it resembles high density polyethylene in appearance, and to an extent in physical properties. Although *trans*-polybutadiene cannot be oriented by cold stretching, strong filaments can be prepared by drawing the polymer at 100° C. The presence of unsaturation in the chain permits vulcanization.

Polybutadiene of 90 per cent *trans* configuration is much less crystalline than pure *trans*-polybutadiene. In its ability to be cold-drawn several hundred per cent, in its hardness, and in its melting point (ca. 65° C) this polybutadiene resembles gutta percha (naturally occurring *trans*-polyisoprene). Although the

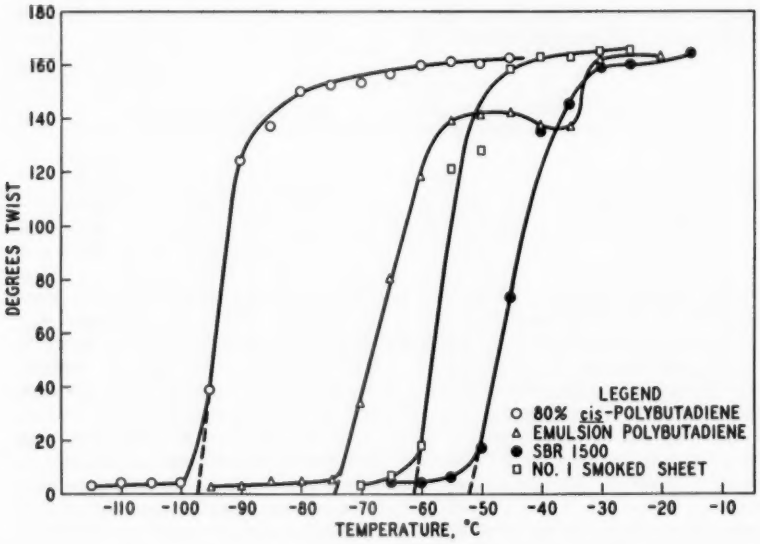


FIG. 9.—Gehman freeze points.

TABLE VII

PROPERTIES OF GUM VULCANIZATES OF VINYL POLYBUTADIENES AT 80° F

	Amorphous polybutadiene, 94% vinyl	Amorphous polybutadiene, 85% vinyl	Syndiotactic polybutadiene, 70% vinyl
Mooney viscosity, ML-4	65	36	Too high to measure
300% modulus, psi	220	190	690
Tensile strength, psi	390	320	1160
Ultimate elongation, %	470	520	470
Shore A hardness	32	32	51

raw polymer is still quite crystalline at room temperature; the tendency to crystallize can be largely suppressed by vulcanization. Tread vulcanizates of 90 per cent *trans*-polybutadiene are tough rubbers characterized by high tensile strength and modulus, excellent elongation, and fair dynamic properties. The physical properties of polybutadienes of this type are discussed in detail in a previous publication[1].

Crystallinity of *trans*-polybutadiene decreases steadily as *trans* content is lowered and for polymers with between 75 and 65 per cent *trans* configuration, it is relatively low at room temperature. However, in spite of the low crystallinity in this type of polybutadiene the raw polymers are thermoplastic. After vulcanization, room temperature crystallinity disappears altogether and the polymers appear suitable for application in tire treads. The dynamic properties of predominantly *trans*-polybutadiene tread stocks compare roughly with those of cold rubber. Resistance to abrasion is good. For instance, a 66 per cent *trans*-polybutadiene of 23 ML-4 Mooney viscosity displayed excellent processability and gave a treadwear rating of 106 relative to cold rubber in retread tire testing.

VINYL POLYBUTADIENE

Figures 3 to 8 show that changes in vinyl content cause relatively small differences in properties for amorphous polymers of approximately equal extent of *cis* and *trans* configuration. However, as already pointed out, any ordered

TABLE VIII

PROPERTIES OF BLACK-REINFORCED VINYL POLYBUTADIENES

	Amorphous polybutadiene, 84% vinyl	Amorphous polybutadiene, 95% vinyl	Crystalline polybutadiene, 70% vinyl
	Original		
300% modulus, psi	2210	1960	2750
Tensile strength, psi	2680	2600	3760
Ultimate elongation, %	340	380	420
Tensile strength at 200° F, psi	840	980	1450
Shore A hardness	65	66	69
Resilience, %	56	62	69
Heat buildup, ° F	37	59	55
NBS abrasion, rev/mil	10.5	7.7	9.2
	Aged 24 hours at 212° F in an air oven		
300% modulus, psi	2500	2550	3400
Tensile strength, psi	2570	2630	3600
Ultimate elongation, %	290	310	320
Resilience, %	53	65	69
Heat buildup, ° F	37	58	53

arrangement of vinyl units will produce marked differences in many physical properties. For the purpose of illustration we have selected three high-vinyl polybutadienes for detailed discussion: (1) 85 per cent vinyl, amorphous polybutadiene, (2) 70 per cent vinyl, syndiotactic polybutadiene and (3) a high molecular weight 94 per cent vinyl polymer.

The mechanical properties of gum vulcanizates of amorphous polybutadienes (Table VII) are indicated by the fact that the polymers with 85 and 94 per cent vinyl unsaturation have modulus values of about 200 psi and tensile strengths of 300–400 psi. However, for the syndiotactic polybutadiene these values are increased threefold. This effect is not due to high molecular weight, as might be inferred from the Mooney viscosity determinations; a significant ML-4 cannot be measured because of residual crystallinity at the temperature of the test. The effect of crystallinity is also reflected in the usually high Shore hardness.

As shown in Table VIII, some of the unusual and interesting properties which appear in the gum vulcanizates are retained in the HAF black reinforced stocks. While the tensile properties of both the 85 and 94 per cent vinyl polybutadienes are ordinary and inferior to those of *cis*-polybutadiene, those of the syndiotactic, 70 per cent vinyl polymer are exceptionally good. On the other hand, there is relatively little difference in Shore hardness or laboratory abrasion resistance between the amorphous or syndiotactic samples.

In dynamic properties the 94 per cent vinyl polybutadiene exhibits an unusual combination of low heat buildup and apparent low resilience. The heat generation is about that obtained with *cis*-polybutadiene or natural rubber and much less than for SBR 1500. Resilience at room temperature is only 56 per cent but rises to 74 per cent at 176° F. The explanation may be that the normal balance of low heat buildup and high resilience is achieved at the temperature reached by the polymer during measurement of heat buildup. In spite of the low unsaturation in the polymer backbone, ozone resistance of the high vinyl polybutadienes was no better than emulsion polybutadiene or SBR 1500.

ACKNOWLEDGMENT

We are indebted to C. W. Strobel for preparing some of the polymers, to L. V. Wilson for the x-ray diffraction patterns, and to V. Thornton, R. S. Silas, and Joy Yates for microstructure determinations.

SUMMARY

The physical properties of polybutadiene vulcanizates have been measured as a function of polymer microstructure. Although the over-all properties of any one polybutadiene are determined by the relative ratio of *cis*, *trans* and vinyl units in the polymer chain, marked changes in physical properties do not occur until a relatively pure configuration is approached or unless the raw polymer displays crystallinity. Thus, polybutadienes containing more than 85 per cent *cis*, *trans* or vinyl units are characteristically different from each other and the differences are accentuated as the isomeric forms approach 100 per cent of a given configuration.

Polybutadiene of 95 per cent *cis* configuration displays very low heat generation and high resilience (equaling natural rubber in these properties) and excellent abrasion resistance. *trans*-Polybutadiene (90 per cent), a crystalline plastic in the raw state, becomes rubbery after vulcanization. Gum vulcanizates

possess high tensile strength, and tread stocks display high modulus and tensile strength, high hardness and fair hysteresis properties. Vulcanizates of amorphous 94 per cent vinyl polybutadiene are characterized by fair tensile properties, low hysteresis, and poor low temperature properties. Crystalline syndiotactic polybutadiene, 70 per cent vinly, displays much higher gum and tread tensile strengths than its amorphous counterpart. Amorphous polybutadienes containing less than 70–80 per cent of any one configuration are generally similar in most properties, and resemble emulsion polybutadiene in many respects.

The wide range of properties of the various polybutadienes makes them suitable for many applications. *cis*-Polybutadiene is an excellent tire rubber, which has given as much as 40 per cent greater abrasion resistance than natural rubber in passenger tire tests. Heavy duty 10:00 × 20 truck tires fabricated with a 1:1 blend of *cis*-polybutadiene and natural rubber in the treads have given slightly better abrasion ratings and lower running temperatures than control tires fabricated entirely from natural rubber. Amorphous 80 per cent *cis*-polybutadiene has been found to possess exceptionally good low temperature properties, far superior to present arctic-type unsaturated elastomers. *trans*-Polybutadienes by virtue of their high modulus, high tensile strength, and high hardness could be utilized in the preparation of hard rubber goods, floor tiles, and shoe soles.

While none of these polybutadienes is yet available commercially, their unusual properties and potential applicability in many areas should lead to their manufacture in the future.

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INFRARED SPECTRA OF CURED AND UNCURED RUBBERS *

G. A. Blokh and A. F. Mal'nev

The newest physical-chemical methods of research enlarge the scope of study of the vulcanization process[1–5]. There is a possibility of studying the structure changes during vulcanization of rubber by the application of infrared spectroscopy[6].

Infrared rays are selectively absorbed. Therefore the infrared absorption spectrum can be used as a characteristic property of a substance and could be used for analytical purposes. The large spectral range of the infrared rays indicates their importance for the study of the properties and structure of substances; this makes possible the determination of the moments of inertia of atomic nuclei and molecules, isotopic mass, arrangement and strength of atomic bonds in the molecule and the frequencies of their vibrations. By knowing the frequencies for pure substances, molecular analyses of complicated mixtures of various organic rubbers, accelerators and other substances could be performed.

The study of linear absorption spectra is the basis of the spectrographic method in the infrared region. Since the frequencies of near infrared radiation correspond to the characteristic frequencies of the atoms in the molecules, this method could be used to obtain interesting information concerning the structure of organic molecules, the chemical structure of high molecular weight compounds, the determination of the presence of specific groups or atoms in the rubber molecule, the character of the bonds between these groups and the order of arrangement of the individual chain links. This is true because the position of the absorption bands, which are specific for a given group of atoms, is practically the same for the different combinations in which the group occurs.

The complicated process of polymerization of diene and vinyl compounds and the structure of different types of rubbers can be investigated with the aid of infrared spectroscopy. For example, Table I lists the characteristic absorption frequencies in the infrared region for some important chemical combinations[7].

In order to determine the presence of absorption at different frequencies the intensity of the monochromatic infrared beam which falls on the sample is compared with the intensity of the beam which is transmitted through the sample. According to Beer's law, the intensity of the electromagnetic radiation transmitted by a medium is determined by the formula

$$I = I_0 e^{-kcx}$$

where I = intensity of the transmitted radiation, I_0 = intensity of the incident radiation, k = specific absorption coefficient which is a function of the frequency, characteristic for each kind of molecule, c = concentration, x = thickness of the absorption layer.

* Translated by Theodor Tarasjuk, Katherine and Willard P. Tyler for Rubber Chemistry and Technology from *Legkaya Promyshlennost*, No. 4, 38–44 (1956).

If we call the transmittance, $T = I/I_0$, then

$$\ln 1/T = kcx$$

By measuring the transmittance, T, with a spectrograph, the value of kc, and of k for the material without solvent ($c = 1$), can be determined if the thickness of the layer, x, is known.

To study the absorption spectrum of a high polymer material, a thin film (15–50 μ) is deposited from solution on a sodium chloride plate which can be put in the spectrograph. The diagram obtained by the spectrographic recorder

TABLE I

Type of bond (absorbing structure)	Characteristic frequency, cm^{-1}	Compound on which determination was made
C—C	993	C_2H_6
C—O—	1034	CH_3OH
C=C	1623	$CH_2=CH_2$
C=O	1744	
C—N	1045	CH_3NH_2
C=N—	1653	$CH_3CH=NOH$
C≡N	2089	HCN
C≡C	1975	$CH \equiv CH$
C—H	2915	CH_4
SH	2597	CH_3SH
—CH=CH_2	910–990	Rubbers: SKB; SKS; SKN,
—CH=CH—	968–975	Rubbers: NK; SKB; SKS; SKN
—C(=CH_3)=CH—	836	Natural rubber
—C(=Cl)=CH—	825	Chloroprene rubber

presents two curves of transmitted energy as a function of wavelength: (1) for the compound studied and (2) for the blank sodium chloride plate. The relative transmission (absorption) for each wavelength is determined by the measurement of the relation of the ordinates of the sample curve to the ordinates of the blank curve. After this, by the use of a calibration curve, the linear diagram of relative transmission (absorption) as a function of wavelength is drawn. Under normal working conditions the accuracy of the wavelength in the 2–15 μ region is assumed to be ± 0.01 μ and the percentage of transmitted energy is determined to within 1%.

By using infrared absorption spectra one can determine, without error, for example, the type of rubber from which a rubber compound was prepared, since the spectra of rubbers are characteristic and can be obtained experimentally.

Figure 1 shows the absorption spectra of natural and synthetic rubbers. By analysis of the spectra we can draw a number of conclusions which will enable us to identify the different types of rubbers[8].

Natural and chloroprene rubbers differ from the other types by the presence of a wide band in the 12 μ region. They differ from each other in the exact

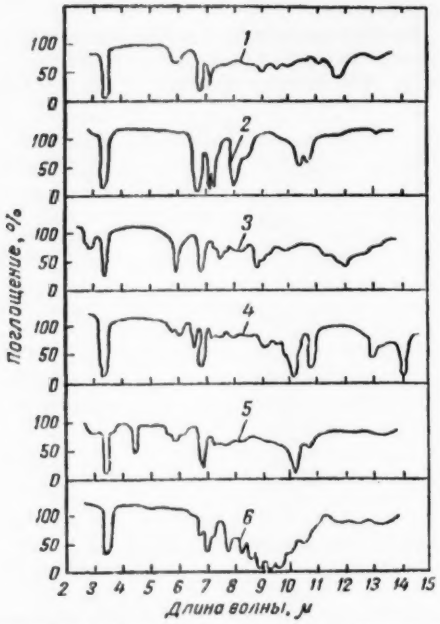

FIG. 1.—Absorption spectra of rubbers. Abscissa, Wavelength, μ; Ordinate, Transmission, %. *1*—Natural rubber; *2*—Butyl rubber; *3*—Chloroprene rubber; *4*—Styrene rubber (SKS); *5*—Nitrile rubber (SKN); *6*—Polysulfide rubber (Thiokol).

position of the band; natural rubber band at 11.95 μ (836 cm^{-1}) for the

$$\begin{array}{l} CH_3 \\ | \\ -C{=}CH- \end{array}$$

group, and the chloroprene rubber band at 12.1 μ (825 cm^{-1}) for the

$$\begin{array}{l} Cl \\ | \\ -C{=}CH- \end{array}$$

group. There are also differences with respect to the nature of the 7.25 μ (1382 cm^{-1}) band of natural rubber, the intensity and position of the 6 μ (1666 cm^{-1}) band characteristic of C=C, and the most characteristic absorption band for chloroprene rubber at 8.94–9 μ (1116–1111 cm^{-1}).

Butyl rubber differs in that it possesses an intense specific band at 8.13 μ (1228 cm^{-1}), characteristic of the internal quaternary carbon atom, and the intense doublet at 7.2 and 7.3 μ. The small amount of isoprene copolymerized with the isobutylene in order to make the rubber vulcanizable is not sufficient to show absorption, so the spectrum of butyl rubber is identical with that of pure polyisobutylene (Oppanol).

SKN (butadiene-nitrile) and SKS (styrene-butadiene) rubbers possess intense bands specific for butadiene polymers at 10.3 μ (968–972 cm^{-1}) characteristic of the —CH=CH— group (1–4 addition) and at 10.9 μ (916 cm^{-1}) for the $—CH=CH_2$ group (1–2 addition). SKS (styrene-butadiene) rubber is easily identified by the characteristic phenyl group bands at 6.23, 6.70 and 14.3 μ. SKN rubber is readily identified by the band at 4.47 μ (2232 cm^{-1}), the characersitic frequency of $C\equiv N$ (nitrile group). Thiokol is characterized by a series of bands at 8.36, 8.64, 8.89, 9.32 and 9.68 μ. Thus, any type or mixture of types of rubbers can be identified by comparison of absorption spectra.

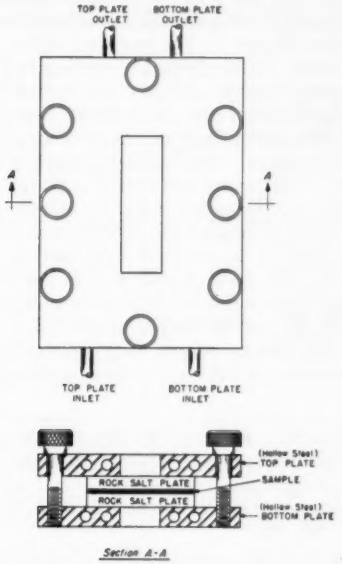

FIG. 2.—Press form for the vulcanization of films under pressure and for taking absorption spectra of samples.frame;

Infrared spectroscopy has been used for measurement of absorption spectra and identification of accelerators[9]. The accelerator in suspension in liquid paraffin is deposited on a rock salt plate. The frequencies of the absorption bands for widely used accelerators have been determined: tetramethylthiuram disulfide—1514 cm^{-1}; zinc diethyldithiocarbamate—1413 and 1502 cm^{-1}; tetraethylthiuram disulfide—1427 and 1502 cm^{-1}; piperidinium pentamethylenedithiocarbamate—1412 cm^{-1}; mercaptobenzothiazole (MBT, Captax)—1425, 1495 and 1594 cm^{-1}; benzothiazolyl disulfide (MBTS, Altax)—1430 and 1590 cm^{-1}; benzothiazolyl-N-cyclohexylsulfenamide (Santocure)—1431 cm^{-1}.

From the technical standpoint it is important to study the structure changes in rubber during the process of oxygen (thermal) and sulfur vulcanization by the use of infrared spectroscopy. In the experiments performed in 1953 we attempted to explain the effect of oxygen, sulfur and accelerators on the structure changes in rubber during the vulcanization process in an air cure, without pressure, and in a press cure.

Two percent solutions of natural, sodium-butadiene and butadiene-nitrile rubbers in benzene were prepared, alone and also in the presence of an antioxidant (Neozone), a vulcanizing agent (sulfur) and accelerators (MBT, thiuram, DPG). The solutions were poured on the surface of rock salt plates to form films 50 μ thick. The films were formed by slow evaporation during 24 hours. Then the prepared films of rubber on the plates were heated in a special thermostated oven in an air or nitrogen atmosphere at normal pressure at 145° for 60–180 minutes. After one hour of heating at 145° the infrared absorption spectra were observed at room temperature. Then the same films were heated at 145° for 120 minutes and again put in the spectrograph.

For the study of the absorption spectra of rubbers cured by press vulcanization a special press form (Figure 2) was prepared with a cutout for the passage of the light beam. Figure 2 is a schematic drawing based on the rather indistinct photo in the original Russian article. The sample of rubber mixture was pressed between two parallel rock salt plates in the press form by means of bolts. In this case, as in technical vulcanization, excess of air and direct contact of the plates with air was eliminated. Only adsorbed oxygen could take part in the vulcanization process. The press form with the plate was put in the oven at 145° for 6 hours. The plate assembly was later put in the spectroscope at room temperature. Infrared absorption spectra were recorded on the VIKS-MZ apparatus. The film to be studied, prepared on the plates of natural salt crystal and heated in the oven, was secured in the holder and placed in the beam of light in front of the entrance slit of the spectrograph. The infrared spectra were studied in the 4.22 to 13.22 μ (2369-750 cm^{-1}) region.

As a result of the stepwise heating of SKB which was unprotected by antioxidant, for 60–180 minutes at 145°, the following changes occurred in the absorption spectra.

1. A new band appeared in the 1739–1675 cm^{-1} region. This establishes the occurrence of an oxidation process and the formation of oxygen containing rubber compounds. It is known[10] that the carbonyl group, C=O, has bands characteristic of the compound in which it occurs: 1727–1703 cm^{-1} for aldehydes, $R-\overset{\overset{O}{\|}}{C}-H$; 1721–1669 cm^{-1} for ketones, $R-\overset{\overset{O}{\|}}{C}-R_1$; 1760–1721 cm^{-1} for keto ethers, $R-\overset{\overset{O}{\|}}{C}-OR_1$. Comparison of the bands obtained in our case in this frequency region with the above data shows that under the conditions of air thermal treatment (without a special oxygen atmosphere) SKB forms oxygen compounds of the aldehyde, ketone, ether and other types. That is, polar groups are formed that are centers for intermolecular reaction. The formation of these compounds was observed by means of spectra[11] in the study of the kinetics of the oxidation of rubber.

2. After three hours heating a band appeared at 1187 cm^{-1}, indicating that ether groups were appearing in the rubber (the characteristic band for the —C—O—C— group lies in the 1248–1111 cm^{-1} region).

3. After the three hour heating the 972 cm^{-1} band disappears. This shows the participation of the —CH=CH— and $-CH=CH_2$ groups in the structure formation and the destruction process taking place on heating SKB which is not tected by antioxidant. SKB protected by antioxidant does not show any pro-

noticeable change in absorption spectrum when heated under the same conditions.

This example clarifies fully the role of the antioxidant, in the presence of which the oxidation process proceeds very slowly. During the three hour heating period the intense bands characteristic of oxygen compounds did not appear.

The absorption spectra of rubber mixtures of SKB with sulfur, with and without antioxidant, were also obtained. Analysis of these spectra revealed that regardless of the presence of antioxidant, three hours heating produces a

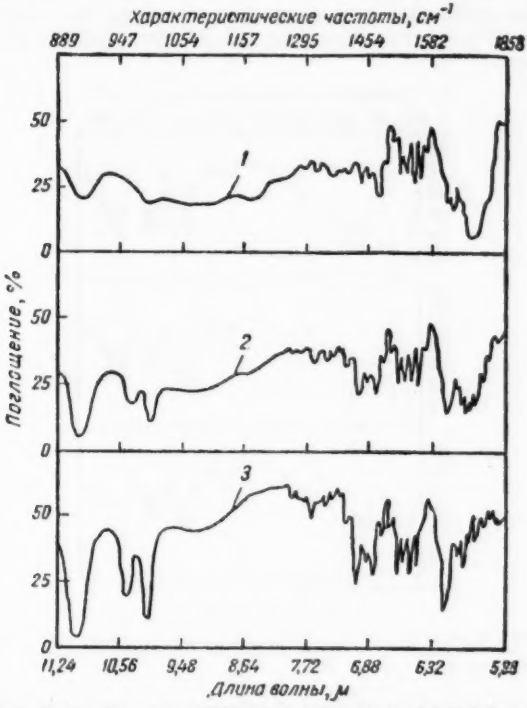

FIG. 3.—Change of absorption spectra of SKB without antioxidant under the influence of heat. Abscissa, Characteristic frequency, cm^{-1}; Wavelength, μ. Ordinate, Transmission, %. *1*—Three hours heating at 145°; *2*—One hour heating at 145°; *3*—Before heating.

strong band in the 1739–1675 cm^{-1} region, characteristic of oxygen compounds containing the C=O group. For evaluation of this fact, attention should be called to the fact that absorption in the same region (5.70–5.95 μ) can also serve as an indication of the formation of thioketoethers, $R—\overset{\overset{O}{\|}}{C}—SR_1$, and thio acids, $R—\overset{\overset{O}{\|}}{C}—SH$; that is, the reaction products of sulfur with the oxygen containing compounds of rubber.

Similar experiments were conducted on vulcanization and thermovulcanization in a nitrogen atmosphere, after which the spectra were run in a nitrogen atmosphere. Under these conditions no changes in the absorption spectra were observed.

Absorption spectra were run of mixtures of SKB with 3% sulfur, 1.5% MBT and 0.5% thiuram, vulcanized for 60–180 minutes at 145°. From a comparison of the observed spectra of the SKB vulcanizates (Figure 4), it was concluded that there was no appreciable effect of heating time on the spectrum of a given mixture. Attention should be called to the fact that in the presence of sulfur and accelerators, the band characteristic of the oxidation process (1727–1675 cm^{-1}), observed during the vulcanization of SKB with sulfur alone, does not appear.

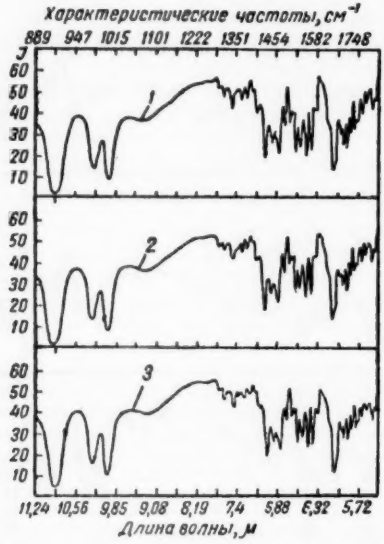

FIG. 4.—Change of absorption spectrum of SKB with antioxidant with heating. Abscissa, Characteristic frequency, cm^{-1}; Wavelength, μ. Ordinate, T. *1*—Three hours heating at 145°; *2*—One hour heating at 145°; *3*—Before heating.

The study of structure changes of butadiene-nitrile rubber, SNK-26, freed from Neozone by alcohol extraction, was carried out by another method. The heating of the films of rubber or its mixtures and the recording of the absorption spectra were done at the same time and temperature. The absorption spectra of SKN-26 were taken on the same sample at 25, 100, 150 and 180°, and then again at room temperature.

The reason for choosing this program was technological. Under production conditions the processing of the rubber causes continual growth of new structure. To the structure formed during mastication of the rubber, new structures are added as a result of mixing, calendering, extrusion and vulcanization. Therefore, the spectra on each sample were taken before and after heating from 25 to 100°, from 100 to 150° and from 150 to 180°. The samples were heated for 15 minutes in each region at which time the upper temperature limit was

reached. The spectrum was then taken for the next 45 minutes without removing the sample from the apparatus. The total time of heating was three hours.

An analysis of the absorption spectra of SKN-26 rubber obtained by this heating program (Figure 5) leads to the conclusion that the more the rubber is

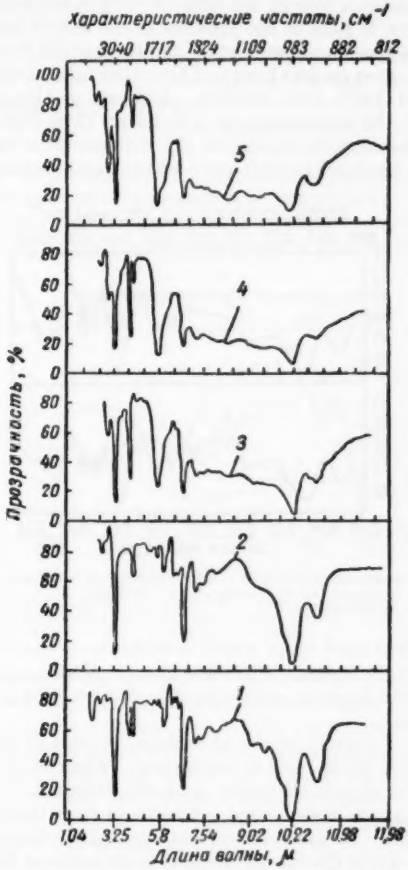

FIG. 5.—Change of absorption spectrum of butadiene-nitrile rubber (SKN-26) as a function of temperature, stepwise heating. Abscissa, Characteristic frequency, cm^{-1}; Wavelength, μ. Ordinate, Transmission, %. *1*—Before heating; *2*—At 100°; *3*—At 150°, *4*—At 180°; *5*—After cooling from 180°.

heated, the greater the band intensities in the 1744–1724 cm^{-1} region, characteristic of the C=O group. The greatest intensity of this band is reached during the 150–180° interval and it does not disappear on cooling. There is a change in the absorption in the 1034–1200 cm^{-1} region, characteristic of the ether group, which is evidence of the course of the structure forming process in which oxygen takes part. There are also pronounced changes in the intensity of the

965–980 cm^{-1} band, for the —CH=CH— group, indicating the participation of double bonds in the structure changes of SKN-26 during vulcanization.

The absorption spectra of mixtures of SKN-26 with 10% sulfur before and after heating three hours at 145°, in contrast to the absorption spectra of SKB with sulfur, do not show the intense 1727–1721 cm^{-1} band. It is known that SKN possesses resistance toward the effect of oxygen as a result of the presence of the nitrile groups, in spite of the presence of the double bonds.

The absorption spectra of two films of mixtures of SKN with 6% sulfur and 1.5% MBT, one heated for one hour and the other heated without interruption for three hours at 145°, were studied. Analysis of the absorption spectra (Figure 6) shows: the appearance of a band at 1748–1658 cm^{-1} after three hours heating, indicating the formation of C=O groups in the rubber; the disappearance of the band in the 1041 cm^{-1} region and a considerable decrease in

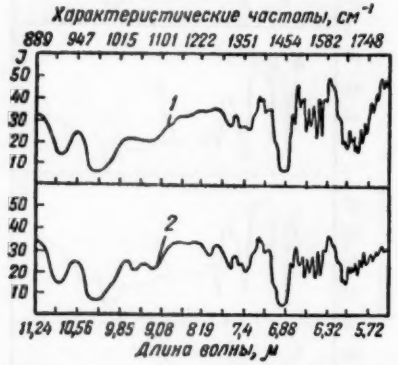

FIG. 6.—Change of absorption spectrum of rubber compound of butadiene-nitrile rubber (SKN-26). Abscissa, Characteristic frequency, cm^{-1}; Wavelength, μ. Ordinate, *T*. *1*—After uninterrupted three hour heating at 145°; *2*—Before heating.

intensity of the 1240 cm^{-1} band which is evidence of the destruction of some oxygen groups and the formation of ether groups; that is, evidence of structure formation. The one hour vulcanization does not produce these changes in the absorption spectrum.

The results of the study of the absorption spectra of natural rubber vulcanized in air and in press cures is interesting. Figure 7 gives the absorption spectra of mixtures of natural rubber with 3% sulfur, 1.5% MBT and 0.5% thiuram. The mixtures were heated 1–6 hours in air without pressure or in the press under pressure. As can be seen from Figure 7 the spectra differ markedly from each other. Even the sample heated for six hours at 145° in the press did not show the bands characteristic of oxygen compounds. In the open air cure, after three hours the spectra showed disappearance of a number of bands in the 12.17–11.87 μ (822–840 cm^{-1}) region and in the 11.24 μ (889 cm^{-1}) region. This indicates that the double bonds of the —CH=CH— and —CH=CH_2 groups, whose characteristic bands lie in these regions, take part in the structure changes during vulcanization. An intense band appears at 1658–1748 cm^{-1}, characteristic of the appearance of oxygen compounds containing the C=O group. Deformation of the bands at 1015–1154 cm^{-1} indicates the formation of hydroxyl groups in the structure of the rubber.

Thus, the spectra show that in a press cure the characteristic bands connected with the formation of oxygen compounds do not appear in six hours of heating. In an open air cure the formation of oxygen containing groups occurs after only 2–3 hours heating.

In separate experiments it was determined that the addition of 0.5% acetone, $\left[\begin{array}{c} CH_3 \\ | \\ CH_3—C=O \end{array}\right]$, to benzene causes the appearance of the characteristic band for the C=O group. This demonstrates the fact that the apparatus is sensitive to small quantities of oxygen.

In the frequency region studied the formation of C—S—C and SH bonds was not observed.

The spectra of unvulcanized and vulcanized rubber differ from each other largely because the vulcanizates possess high absorption. This is evidence of the increase of density of the structure (molecular weight). An analogous situation was observed in a homologous series of hydrocarbons. The practi-

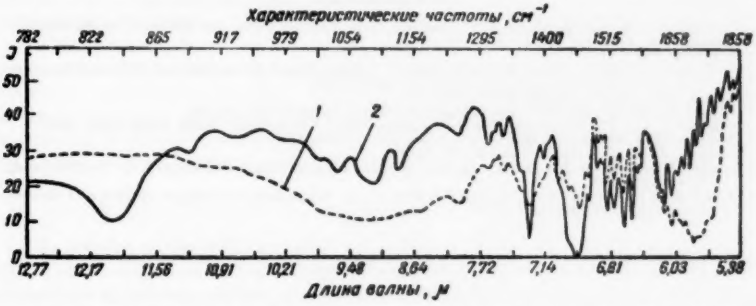

FIG. 7.—Change of absorption spectra of compounds of natural rubber as a function of time of heating and pressure. Abscissa, Characteristic frequency, cm^{-1}; Wavelength, μ. Ordinate, T. *1*—Air cure without pressure, 3–6 hours at 145°; *2*—Press cure, 1–6 hours at 145°.

cally identical spectra of rubber and its vulcanizates does not contradict the modern point of view that comparatively small quantities of crosslinks (chemical, hydrogen bonds, polar reactions, and others) are produced during the formation of the three dimensional network in the vulcanization process. Since the infrared spectra of polymers are determined almost exclusively by the small repeated structure units and not by the overall configuration of the chain, the effect of vulcanization, in which the structure changes take place in a comparatively small number of the repeating polymer units, apparently can not affect the rubber spectra.

It is known that accelerators not only actively influence the kinetics of vulcanization but also enter into the structure by reaction with the rubber[5]. It is interesting to observe this with the help of absorption spectra. 1.5, 6 and 10% MBT were introduced into SKN rubber. After heating at 145° for 1, 2, and 3 hours the absorption spectra of the samples were taken. The introduction of 6–10% MBT causes the appearance of three new bands at 1015, 1033 and 1101 cm^{-1}. After the first hour of heating the 1015 cm^{-1} band disappears, while the other two bands remain after three hours of heating. The addition of 6% DPG caused the formation of two new bands in the 1077–1033 cm^{-1} region which

remained after two hours of heating. The introduction of 6% thiuram did not produce new bands under the same conditions of thermal treatment.

On introducing accelerators into SKB rubber, the following results were obtained: 2% MBT did not cause a change in the absorption spectrum; the addition of 2% MBT in SKB containing no antioxidant did not cause the appearance of any new bands on heating (Figure 3); the introduction of 6% DPG in SKB with antioxidant resulted in the appearance of a new band connected with oxidation and formation of C=O groups (1727 cm^{-1}) and also deformation of the 947–975 cm^{-1} band; the addition of 6% MBT ot SKB with antioxidant followed by 1–3 hours heating produced the above phenomena to an insignificant degree.

It is understandable that all of these data can not be explained exactly, but they undoubtedly indicate that accelerators have an active influence on the structure changes occurring in rubber during vulcanization.

Thus, infrared spectroscopy should find wide application to research on technological processes.

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STRUCTURE AND PROPERTIES OF FILLED STOCKS XVI. POLYBUTADIENE FILLED WITH COLLOIDAL SILICA *

B. Dogadkin, K. Pechkovskaya, and E. Gol'dman

In our previous papers[1–5] the investigation of filler distribution in rubber was described and it was shown that active fillers in certain concentrations form thixotropic chain structures. Many physico-mechanical properties of vulcanizates such as wear resistance, conductivity, heat buildup, etc. are affected by the degree to which such structures are present. The structural changes of carbon black vulcanizates under the influence of heat and mechanical action were also investigated.

In the present paper results of similar investigations with rubber stocks containing colloidal silica are reported. This choice was made because it is possible by different processes to obtain from the same starting material, silica samples with very much different reinforcing properties. Thereby it should be possible to compare active and inactive fillers which are more closely related than those previously investigated.

MOISTURE CONTENT AND ACTIVITY OF COLLOIDAL SILICA

The results of the chemical analysis (SiO_2 content, sesquioxide, moisture, alkali, etc.) and physico-chemical analysis (specific surface, pH, specific weight, adsorption of toluene, stearic acid and rubber) vary approximately within the same limits for silicas of varying activity (Table I). However, the specimens investigated had very different reinforcing action on rubber. This is demonstrated on examination of vulcanizates made from Na-butadiene rubber containing these silica samples (Table II). However, there is no doubt that the reinforcing ability of colloidal silica should correlate in some way with its adsorptive properties. Blokh, Neimark and others[6] have shown that the most active specimens adsorb the largest amount of moisture, which in turn is easiest desorbed. The less active specimens in turn adsorb considerably less water which in turn is retained more strongly. It is possible that the greater ability to adsorb moisture may be explained by the larger specific surface of the active specimens (the authors give a value for specific surface for one sample only) and the greater ease of desorption by the lower hydrophylicity of the same samples. This is confirmed by the results obtained by Rebinder[7] which established an inverse relationship between the hydrophylicity of "white soot" and its activity as reinforcing agent of rubber. We measured the moisture takeup capacity of colloidal silica from the liquid phase by establishing the quantity of moisture which is adsorbed by a sample on stirring it into water until inversion of phase occurred; this was noticed by an abrupt change of viscosity of the paste. The quantity of adsorbed water will be larger, the larger the specific surface of the powder and the higher its degree of aggregation, since water not only wets

* Translated for Rubber Chemistry and Technology from *Kauchuk i Rezina* 16, No. 9, pages 1–5 (1957).

TABLE I

RESULTS OF PHYSICO–CHEMICAL ANALYSIS OF COLLOIDAL SILICA SAMPLES OF VARIOUS ACTIVITY

Characteristic of filler	% content				Spec. gravity	Spec. surface, m^2/g	% adsorption			pH
	SiO_2	Sesqui oxide	Moisture	Alkaline			Toluene	Stearic acid	Rubber	
Active	82.3	1.3	5.7	2.06	2.0	61.0	13.4	21.5	20.0	8.7
	—	—	3.8	—	—	56.6	9.5	12.0	13.0	8.5
	—	—	3.8	—	—	—	10.0	4.8	9.6	9.1
Medium active	—	—	4.3	—	—	—	21.5	—	—	9.0
	—	—	4.2	—	—	—	14.4	—	—	8.4
	—	—	4.9	—	—	—	11.7	—	—	9.4
Nonactive	—	—	3.7	—	—	—	—	4.8	21.5	9.0
	84.1	1.8	3.7	2.2	2.11	50.3	9.4	16.2	10.5	10.0
	—	—	3.6	—	—	44.6	19.5	10.8	—	9.0

the exposed surface but also fills up space between particles of the aggregate; the value of moisture adsorption capacity must therefore be considered a complex function expressing the specific surface and the structure of the silica aggregate.

Measurement of the moisture capacity of the silica was carried out as follows: the sample of the filler (0.5 g) was placed on a watch glass and water was added slowly from a microburette. After addition of every 2–3 drops of water, the mixture was agitated with a glass rod. This was continued until the sample was completely wetted, when cake formation was observed. The addition of one excess drop of water sharply decreased the viscosity of the cake. The number of ml adsorbed by 0.5 g of colloidal silica is called the water number, analogous to the oil number that expressed the oil adsorption capacity of carbon black. In Table II, values for the water numbers of SiO_2 specimens investigated are given. It is apparent that the reinforcing ability of the specimens is larger, the larger their water number is. This relationship was confirmed on some 200 samples of colloidal SiO_2 (Figure 1). A similar relationship was established between the moisture adsorption capacity of the filler and the modulus of the filled rubber (Figure 2). Thus the water number should be a very useful characteristic for the evaluation of rubber reinforcing properties of colloidal silica.

TABLE II

PHYSICO–MECHANICAL DATA OF VULCANIZATES CONTAINING SPECIMENS OF COLLOIDAL SILICA OF VARIOUS ACTIVITY

No. of samples	Characteristic of filler	Physico-mechanical data					
		Tensile strength, kg/cm^2	Elongation, %		Tear resistance, kg/cm^2	300% modulus kg/cm^2	Water number, mg/g
			Relative	Remaining			
1	Active	115.7	527	34.6	43.3	59.0	1.30
2		115.8	556	30.0	43.0	53.0	1.20
3		118.0	513	32.8	41.5	60.0	1.24
4	Medium	63.0	352	—	36.0	44	1.02
5	active	69.1	452	37.0	34.0	49.0	1.04
6		68.0	352	24.0	35.0	45.0	1.06
7	Inactive	39.4	300	16.0	27.0	27.0	0.85
8		41.3	350	21.4	25.2	44.0	0.90
9		45.0	352	—	25.2	38.0	0.94

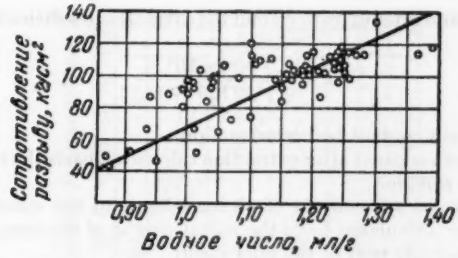

FIG. 1.—Relation between water number (abscissa) in ml/g and tensile strength (ordinate) in kg/cm².

Taking into account the ease and speed of the water number determination, it would be advisable to use this method as a quick control in the manufacture of colloidal silica for the reinforcement of rubber stock.

THE STRUCTURE OF THE RUBBER STOCKS CONTAINING COLLOIDAL SILICA

In order to investigate the distribution of colloidal silica in Na-butadiene rubber we made use of its rate of solution in dilute NaOH. It is possible that the linear and two dimensional structures that made up colloidal silica facilitate penetration of NaOH into the mixture and also the removal of the silicate solution formed. Consequently the better such structures are developed the faster and more complete will be the removal of filler from the mixture on boiling in 1% NaOH solution. In case the filler is distributed as distinct particles or as aggregates which are separated by layers of rubber, the rate of filler removal will depend on the diffusion of the water phase through the rubber.

The following procedure was used for this investigation: The rubber mixtures were prepared on micro mills; sheets of 0.8–1.0 mm thickness were made on a laboratory calender and 2 × 2 cm test samples cut out. These samples were placed into a flask with reflux condenser, containing 100 ml of 1% NaOH solution per two samples; the samples were boiled from 2–20 hours. Every two hours two samples were withdrawn, pressed between filter papers and dried at 100–105° for 1½–2 hours. The dried samples were burned in a muffle furnace for an ash determination. Ash contents were also determined before extraction. The dissolved silica was determined from the difference between the ash

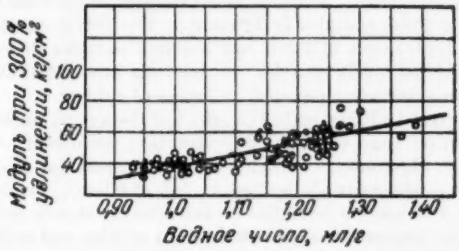

FIG. 2.—Relation between water number (abscissa) in ml/g and 300% modulus (ordinate) in kg/cm².

contents before and after extratioc annd the extraction coefficient k calculated as

$$k = \frac{C_1 - C_2 \cdot 10^6\ \%}{C_1 \cdot P(100 - C_3)}$$

where C_1 = % ash content before extraction.
C_2 = % ash content after extraction calculated basis the initial weight of the sample.
C_3 = % total ash content of all ingredients of the mixture except the filler, calculated basis the initial weight of the sample.
P = % soluble part of the filler itself.

On Figure 3 data are given showing the extraction kinetics of active sample No. 1 made of two component rubber stocks with various filler contents. It is shown that the extraction of active silica from two component stocks begins at

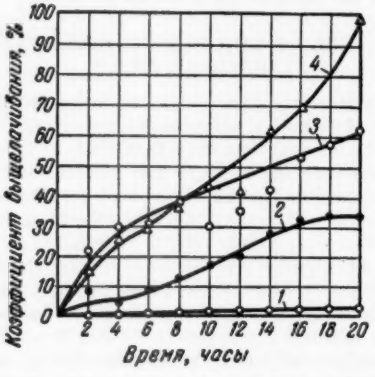

FIG. 3.—Kinetics of extraction of the active silica from the binary mixtures as function of the silica concentration (in vol.% with respect to rubber). *1* =35%; *2* =40%; *3* =45%; *4* =50%. The ordinate is extraction coefficient, %; the abscissa is time, hours.

40% (vol.) of filler in rubber. Below this level extraction of silica is practically negligible, even after a 20 hour reflux period in NaOH solution. Under the same conditions the inactive sample No. 7 is not extractable from two component stocks at any filler level. It follows that the structure of the two component stocks containing these samples is different. The active samples form chain structures with high levels of filler, but inactive samples do not exhibit this phenomenon. At all levels of filler its particles are distributed as isolated entities and aggregates are separated by layers of rubber.

It was of interest to investigate the effect of dispersing agents on the character of distribution (and thus on the extraction coefficient) of the colloidal silica in the same elastomer. Stearic acid was chosen for that purpose and added as third component (technical grade, 5% of filler). From the extraction kinetics (Figure 4) it can be seen that on introducing stearic acid extraction of reinforced samples begins already at 20% (vol.) of filler and at 35% practically all of it is extracted during 10 hours reflux. The dispersing agent also helps to distribute the inactive filler more homogeneously.

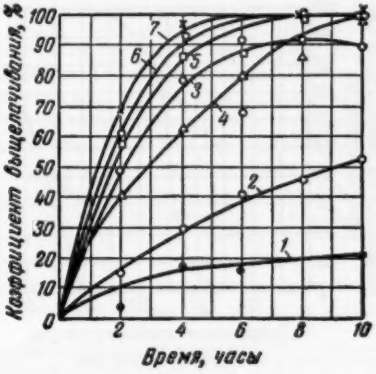

FIG. 4.—Kinetics of extraction of active silica from three component mixtures as function of their silica content (in vol.% with respect to rubber). *1* =20%; *2* =25%; *3* =30%; *4* =35%; *5* =40%; *6* =45%; *7* =50%. The ordinate is extraction coefficient, %; the abscissa is time, hours.

The curves given on Figure 5 show, however, that at all concentrations the extraction coefficient of inactive colloidal silica is considerably lower than of active silica; at filler levels of 40% (vol.) only 2% of inactive silica are extracted in 20 hours while active silica is completely extracted in 8 hours. The extraction coefficients of active and inactive silica as a function of the filler level is shown in Figure 6.

From Figure 6 it becomes apparent that active silica is completely extracted at a level of approximately 35 volumes per 100 parts by weight of rubber, where inactive samples are hardly touched.

To clarify the character of the bond between rubber and filler, samples of the same stocks were swelled in binary solvent (20% toluene and 80% butanol). This solvent combination caused limited swelling of gum stock containing 30% (vol.) filler. Results of swelling experiments (Figure 7) at 40–70° C show that at

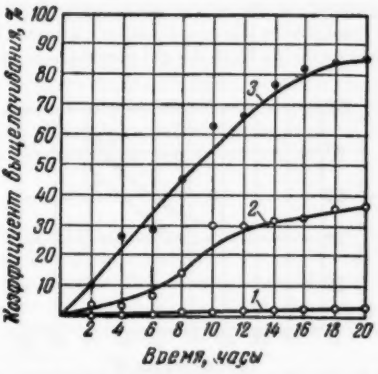

FIG. 5.—Kinetics of extraction of the inactive silica from three component mixtures as function of their silica contents (in vol.% with respect to rubber). *1* =40%; *2* =45%; *3* =50%. The ordinate is extraction coefficient, %; the abscissa is time, hours.

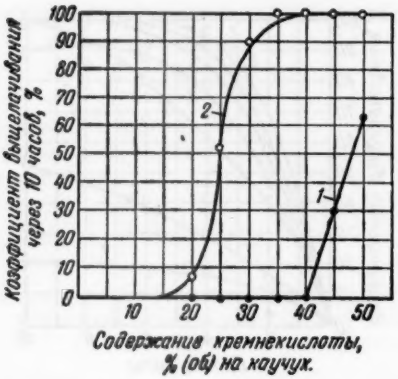

FIG. 6.—Relation between coefficient of extraction and filler content. *1* = mixtures containing inactive silica; *2* = mixtures containing active silica. The ordinate is extraction coefficient after 10 hours, %; the abscissa is silica content, volume % of rubber.

all temperatures swelling is larger in the case of inactive filler samples. Consequently, the number of linkages of the rubber with the active filler is larger than with equal amounts of inactive silica. In most published papers[8–11] the formation of a rubber-filler gel is considered as the result of the interaction of rubber with filler: the decrease of solubility and swelling of the rubber in such systems is entirely blamed on rubber-filler linkages, which have, according to a number of authors[12–14], chemical valence bond character. It seems to us that our own data in this paper on extraction of filler from rubber mixtures and the results of the work of Menadue and Endter[9,15] speak against such one-sided interpretation of the structure of the rubber-filler gel. If, indeed, the formation of insoluble gel should be due solely to bonds between rubber and filler, the initial mobility of the molecules should return upon breaking of those bonds on extraction; this mobility should cause increased solubility of the sample in organic solvents after extraction. This theory was not confirmed by our experiments. After removal of the active silica by extraction, the remaining rubbery portion was insoluble in the usual rubber solvents (benzene, petroleum ether). It is therefore probable that the gel structure is at least partly due to

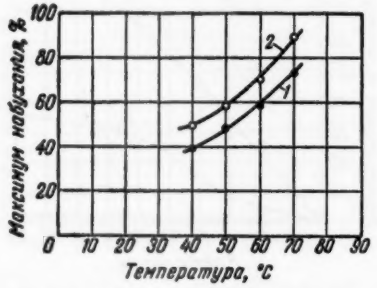

FIG. 7.—Swelling maxima of mixtures (ordinate) in %, containing active (*1*) and inactive (*2*) colloidal silica at various temperatures (abscissa in ° C).

crosslinking between polymer molecules. The bonds may be formed as the result of the interaction of rubber with active materials adsorbed on the surface of the filler such as oxygen and peroxides capable of giving the rubber additional "structure". The fact that the active silica can be completely extracted from the system indicates to us that the linkages between colloidal silica and rubber are of the molecular type rather than chemical valence forces.

As was mentioned previously, it had been established[1–5] that in rubber-carbon black systems the character of the filler distribution essentially determines many physico-mechanical properties of the vulcanizates. The carbon blacks that have a tendency to form chain structures also exhibit the maximum reinforcing effect. The reason for this correlation between reinforcing power and tendency for structure formation was discussed in earlier papers[1–5]. An analogous correlation between structure and physico-mechanical properties is also found in the case of rubber containing colloidal silica ("white blacks" of various

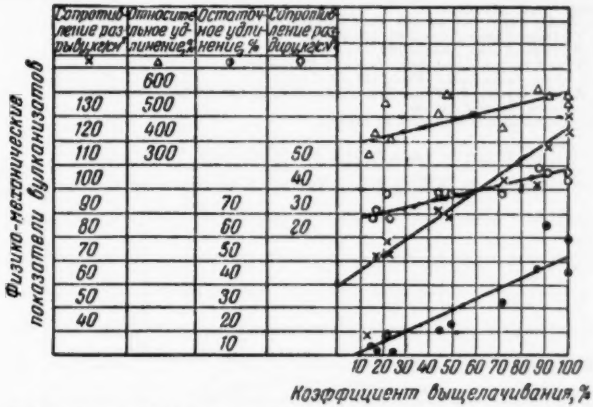

FIG. 8.—Relation between the extraction coefficient (abscissa) in % and physico-mechanical properties of vulcanizates which are given in the four columns at the left of the plots. The headings and plot points from left to right are: tensile, kg/cm², crosses; per cent elongation, triangles; permanent set, %, closed circles; tear resistance, kg/cm, open circles.

activities). As is shown in Figure 8, the larger the quantity of filler extracted, or in other words, the more chain structure the silica exhibits the higher is the durability, elongation and tear resistance of the rubber compound containing this filler. Thus, the extraction method can be used for the evaluation of the quality of the silica as reinforcing agent for rubber.

SUMMARY

1. Colloidal silica can be partially or completely removed from filled rubber stocks by boiling in 1% aqueous NaOH.

2. Degree and rate of extracting directly depend on the reinforcing effect of the silica. The higher the filler activity, the more complete its extractability from the rubber. Inactive samples of silica practically cannot be extracted from filled rubber stocks.

3. The active silica forms a thixotropic chain structure in the rubber, but inactive silica is distributed in rubber as isolated particles or aggregates.

4. The rubber portion that remains after extraction of the active silica is insoluble in common rubber solvents.

5. The equilibrium swelling value in binary solvents (butanol-toluene) is lower, the higher the reinforcing action of the silica.

6. The reinforcing effect of silica is proportional to its moisture takeup capacity, which may be determined by a simple method described.

7. Based on the experiments described, the type of linkages involved and the structure of the rubber stock filled with silica are considered.

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CORRELATION OF ROOM TEMPERATURE SHELF AGING WITH ACCELERATED AGING

R. A. Youmans and G. C. Maassen

R. T. Vanderbilt Co. Inc., New York N. Y.

An article having this title republished in Rubber Chemistry & Technology, Vol. 28, page 1133 (1955) has been found to contain errors with respect to six of the eight figures which it contained. The corrected figures are as follows. The authors are grateful to A. E. Juve for calling attention to the regrettable errors.

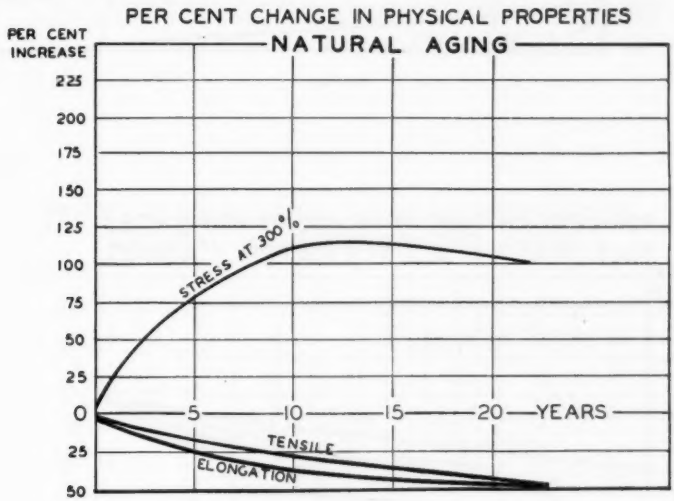
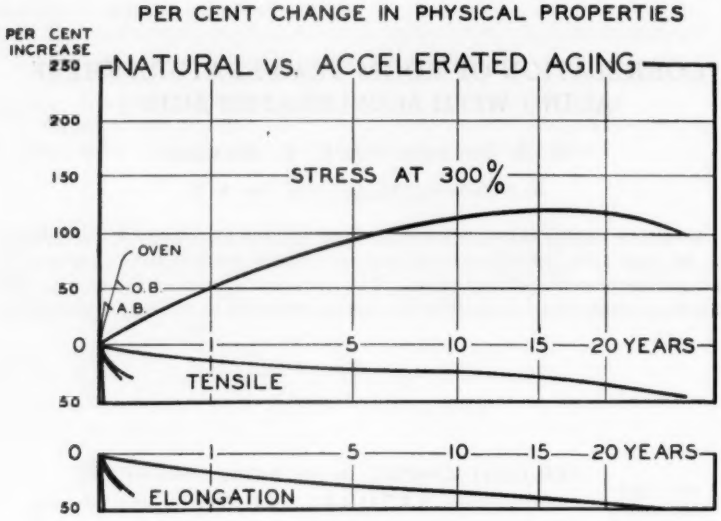


Fig. 1.


PER CENT CHANGE IN PHYSICAL PROPERTIES
PER CENT INCREASE
NATURAL vs. ACCELERATED AGING
250
200
150
100
50
0
50
STRESS AT 300%
OVEN
O.B.
A.B.
1
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1
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20 YEARS
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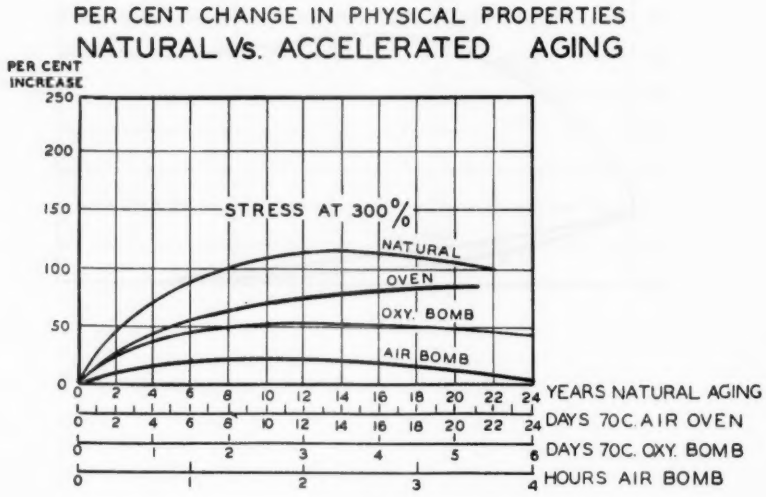
ELONGATION

Fig. 2.


PER CENT CHANGE IN PHYSICAL PROPERTIES
NATURAL Vs. ACCELERATED AGING
PER CENT INCREASE
250
200
150
100
50
0
STRESS AT 300%
NATURAL
OVEN
OXY. BOMB
AIR BOMB
0 2 4 6 8 10 12 14 16 18 20 22 24
YEARS NATURAL AGING
0 2 4 6 8 10 12 14 16 18 20 22 24
DAYS 70C. AIR OVEN
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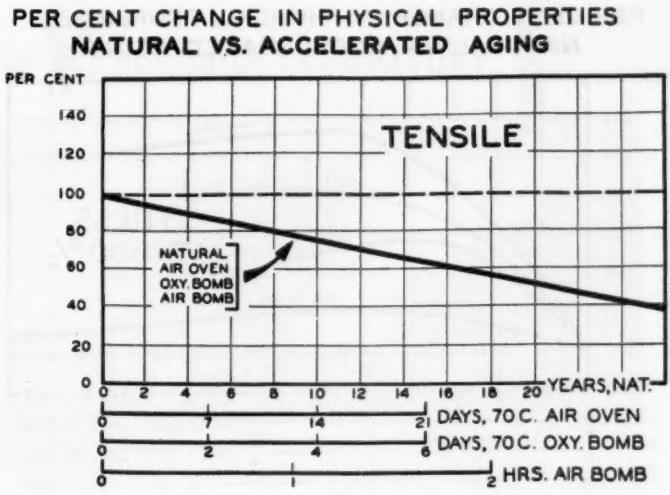
DAYS 70C. OXY. BOMB
0 1 2 3 4
HOURS AIR BOMB

Fig. 5.


PER CENT CHANGE IN PHYSICAL PROPERTIES
NATURAL VS. ACCELERATED AGING
PER CENT
140
120
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80
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40
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AIR OVEN
OXY. BOMB
AIR BOMB
0 2 4 6 8 10 12 14 16 18 20 YEARS, NAT.
0 7 14 21 DAYS, 70 C. AIR OVEN
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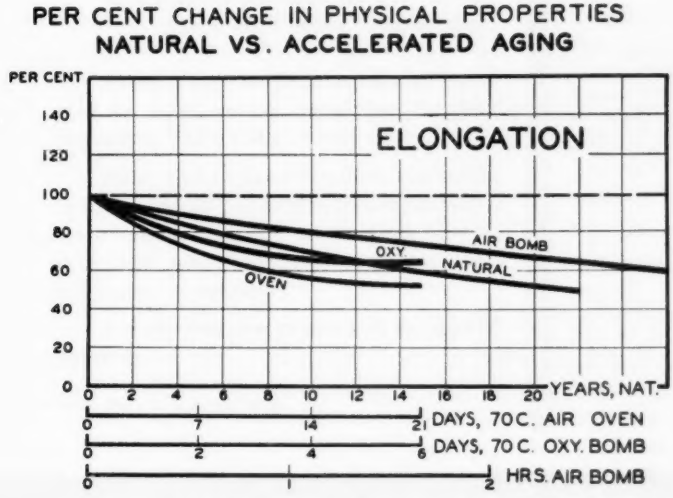
0 1 2 HRS. AIR BOMB

FIG. 6.


PER CENT CHANGE IN PHYSICAL PROPERTIES
NATURAL VS. ACCELERATED AGING
PER CENT
140
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ELONGATION
AIR BOMB
OXY
NATURAL
OVEN
0 2 4 6 8 10 12 14 16 18 20 YEARS, NAT.
0 7 14 21 DAYS, 70 C. AIR OVEN
0 2 4 6 DAYS, 70 C. OXY. BOMB
0 1 2 HRS. AIR BOMB

FIG. 7.

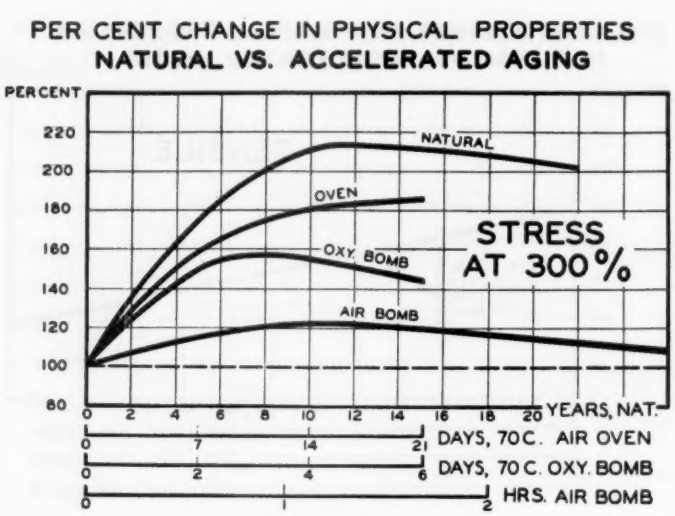
PER CENT CHANGE IN PHYSICAL PROPERTIES
NATURAL VS. ACCELERATED AGING
PERCENT
220
200
180
160
140
120
100
80
NATURAL
OVEN
OXY. BOMB
AIR BOMB
STRESS
AT 300%
0 2 4 6 8 10 12 14 16 18 20 YEARS, NAT.
0 7 14 21 DAYS, 70C. AIR OVEN
0 2 4 6 DAYS, 70C. OXY. BOMB
0 2 HRS. AIR BOMB

FIG. 8.

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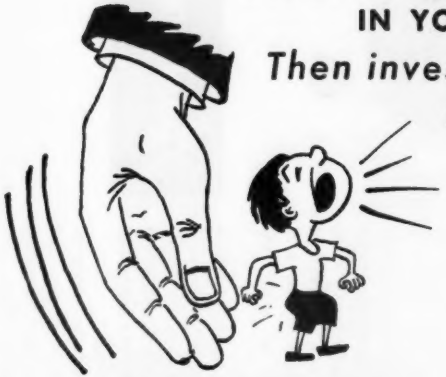

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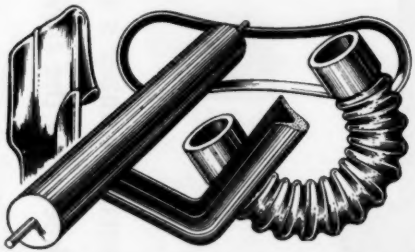

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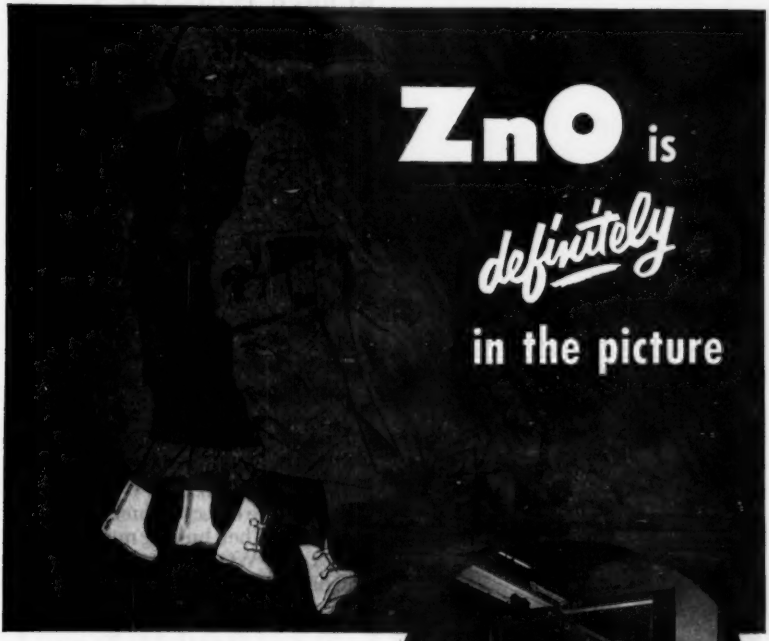

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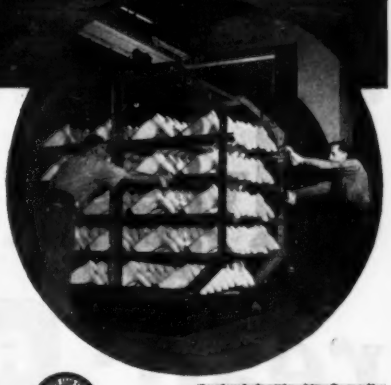

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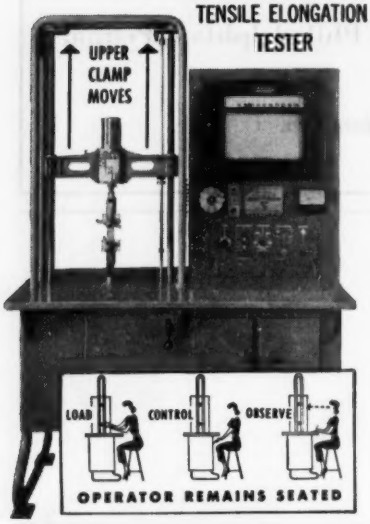

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